The Reactions of Thiolate, Alkoxide, Thioether and Carboxylate Chelate Complexes of Cobalt(III) with Chromium(II)

By

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THE REACTIONS OF THIOLATE, ALKOXIDE, THIOETHER AND CARBOXYLATE CHELATE COMPLEXES OF COBALT(III) WITH CHROMIUM(II)

By

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The reductions of 2-mercaptopropionatobis(ethylenediamine)cobalt-(III) (A), lactatobis(ethylenediamine)cobalt(III) (B), 2-methylthioacetatobis(ethylenediamine)cobalt(III) (C) and glycinatobis-(ethylenediamine)cobalt(III) (D) by chromium(II) were investigated in an effort to ascertain the contributions of sterically hindered mercaptide and alkoxide, terminal thioether and chelated carboxylate functions, respectively, to inner-sphere reactivity parameters. For all reactions the stoichiometry was found to be equimolar in oxidant and reductant. Product analysis indicated all reactions proceeded *via* an inner-sphere pathway.

The reduction of (A) by chromium(II) yielded a second-order rate constant of $1.55 \times 10^5\ \underline{M}^{-1}\ \mathrm{sec}^{-1}$, 25°C, an activation enthalpy of 1.1 kcal/mole and an activation entropy of -31.1 eu. The initial product of the redox reaction was formulated as 2-mercaptopropionatopentaaquochromium(III) (mercaptide-bound) (E). (E) was observed as a fleeting intermediate and converted at an observable rate to 2-mercaptopropionatotetraaquochromium(III) (chelated) (F) ($k = (1.0 + 2.6[H^+]) \times 10^{-2}$ ($\underline{M}$ and sec)). Chelate ring closure is two-fold faster than the analogous system with mercaptoacetate.

The chelate (F) equilibrated with a species characterized as 2-mercaptopropionatopentaaquochromium(III) (carboxylate-bound) (G) ($K_{eq} = 10.5$). Rate constants for ring opening and closure were found to be $k_f = (7.31[H^+]) \times 10^{-5}$ and $k_r = 7.10 \times 10^{-6}$ (M and sec). Comparison to the substituted chelate reveals no significant difference in rates.

Reactivity parameters for the reaction of (B) with chromium(II) were found to be $k = (7.31 + 0.023[H^+]^{-1} / 1 + K_a[H^+]^{-1})$ and $k_2 = 52$ (M and sec), $\Delta H^\ddagger = 4.7$ kcal/mole, $\Delta S^\ddagger = -39.1$ eu ($[H^+] = 1.0$ M). Methyl substitution on the chelate ring was found to decrease the second-order rate constants equally for both mercaptide and alkoxide bridging functions compared to the unsubstituted complexes previously studied.

Reaction of (C) with chromium(II) yielded $k_{obs} = 267$ (M and sec, 25°C), $\Delta H^\ddagger = 8.5$ kcal/mole and $\Delta S^\ddagger = -18.9$ eu. The product of the initial redox reaction underwent at least one and perhaps two observable subsequent reactions, indicating thioether as the bridging function.

Reaction of (D) with chromium(II) yielded $k = 2.22$ (M and sec^{-1}, 25°C), $\Delta H^\ddagger = 8.8$ kcal/mole and $\Delta S^\ddagger = -27.4$ eu. In comparison to monodentate carboxylate cobalt(III) complexes, the presence of carboxylate in a chelate ring was concluded to enhance the ability of the carbonyl function to serve as a bridging ligand.

Reactivity parameters obtained for (A), (B), (C) and (D) are discussed relative to their mechanistic implications.

INTRODUCTION

Although the coordination of metal ions by sulfur in the form of mercaptide, sulfide, or thioether functions have long been known, only during the last decade have their interactions been recognized as vital in biological systems. Metal-sulfur coordination is now known to play key roles in the processes of photosynthesis, nitrogen fixation, oxygen metabolism, hydroxylation of steroidal compounds and electron transport.[1] Also several compounds whose specific biological function has not yet been elucidated are known to have metal-sulfur coordination.[2]

The most explicit demonstration of metal coordination by sulfur has come from recent structural determinations by x-ray crystallography. In clostridial rubredoxin, whose function is unknown, the single iron atom is coordinated tetrahedrally by four cysteinyl mercaptide functions.[3a] Spectral studies indicate that this coordination is retained in solution.[3b] In horse heart and bonito cytochrome *c*, the heme iron is coordinated in the out-of-plane positions by imidazole nitrogen and methionyl thioether functions.[4] Thus the importance of both mercaptide and thioether coordination is definitely established.

Extensive chemical and physical investigations to date have been carried out on members of the class of non-heme iron proteins (NHIP) known as ferredoxins which are involved in photosynthetic and nitrogen-fixation processes.[1,5] The isolation of several proteins of this type has formed the basis of investigation work.[6] In general, the compounds of this class contain stoichiometrically related non-heme iron, cysteine, and acid-labile sulfur, exhibit physical parameters which are anomalous for iron and serve in biological electron transport functions. Specific familial characteristics of ferredoxins are (1) their relatively low molecular weight (~12,000-30,000 g/mole), (2) the presence of acid-labile sulfur (treatment with acid produces H_2S) in an amount approximately equivalent to their iron content, (3) a stoichiometric relationship of iron and cysteinyl ligands, (4) electronic absorption and electron paramagnetic resonance which is anomalous for iron complexes and (5) oxidation potentials (0.2 to 0.4 v at pH = 7) which are unprecedented for iron complexes. Chemical subunits of this class are also incorporated, with other redox functions, into more complex enzymes which are utilized in various biological redox processes.[1]

The presence of both iron and labile sulfur at the active site of a typical two-iron protein was established by epr measurements on isotopically substituted species.[2b] Iron and acid-labile sulfur were removed from the protein to yield the inactive apoprotein. Biological activity was restored by treatment with iron salts in combination with 2-mercaptoethanol and inorganic sulfide. Substitution of selenium for inorganic sulfur also regenerated a substantially active protein.[7] The splitting of the epr signal in the reduced protein by independently substituted appropriate isotopes of iron and selenium established their mutual proximity to the site of reduction. A similar proximity for the cysteinyl sulfur atoms is suggested by the epr behavior of protein produced by organisms grown on an isotopically substituted source of sulfur.[7]

This brief summary is representative of recent research which demonstrates an extensive and varied utilization of metal ions coordinated by thiolate, thioether and "labile" sulfur atoms in biological oxidation-reduction processes. The research to be described here represents an effort to examine the influence of two of these donor functions on the redox behavior of certain metal complexes. The complexes were chosen not for the extent to which they simulated the biological examples but rather for their virtue of incorporating certain of the biological aspects into systems whose reactions stood the best chance of being both thoroughly characterized and interpreted in relationship to prior fundamental studies. This objective stands in contrast to the alternative approach of investigating systems more directly related to those found biologically. However, the iron(III)mercaptide complexes suggested by the biological systems are complicated, unstable and kinetically labile,[8] leading to less than definitive results. Simple complexes with iron-thioether coordination have proved elusive to synthesis and would likely present a low susceptibility to thorough kinetic description.

The reactions described herein serve as model systems in only the most rudimentary sense that they do incorporate the biological type of donor functions as ligands. The possibility of substantial differences between the reactivity patterns delineated here and those of the biological examples is openly anticipated; nevertheless, a better understanding of how these ligands affect oxidation-reduction behavior should shed some light on the reasons for their extensive biological utilization.

One approach to evaluating the effects of mercaptide and thioether coordination involves the study of well-characterized complexes whose reactions are susceptible to detailed mechanistic investigation. Further, monomeric, inert complexes of cobalt(III) or chromium(III) containing a single coordinated mercaptide or thioether function appeared desirable in the initial studies for comparative purposes with earlier work. With these objectives, a research project in these laboratories resulted in the preparation and isolation of $[Co(en)_2(OOCCH_2S)]ClO_4$.[9] For the purpose of comparing the reactivities and mechanistic patterns an analogous compound with the sulfur replaced by a more classical oxygen donor atom was prepared, $[Co(en)_2(OOCCH_2O)]ClO_4$.[9] For the pair of complexes, the behavior toward chromium(II) and $[Ru(NH_3)_6]^{2+}$ as typical inner-and outer-sphere reductants, respectively, as well as applicable substitutional behavior of the reaction products was examined.[9,10] This marked the first significant development in evaluating the influence of a coordinated mercaptide in oxidation-reduction reactions.

In order to consider these results and those described herein it is necessary to recognize the two general categories which have been established for oxidation-reduction reactions of transition metal complexes in solution, that is, the inner-sphere and outer-sphere mechanisms.[11] For the inner-sphere reaction, the two reacting metal centers are joined in the activated complex *via* a ligand common to the first coordination spheres of both metal ions. An outer-sphere reaction is characterized by an activated complex in which no sharing of ligands occur, that is, the primary coordination spheres of the respective metal ions remain intact with no bond cleavage or bond making required for electron transfer.

For an inner-sphere reaction one of the reactants must be sufficiently labile so that ligand substitution involving a ligand from the second reactant can occur prior to electron transfer. The bridging ligand(s) of the second complex is required to have available electron pairs or orbitals of sufficient energy and proper symmetry for forming a bridge between the two metal centers. The bridging ligand brought in by the second reactant must be retained long enough for the electron transfer to occur. By meeting the above requirements an inner-sphere reaction is made possible but not mandatory. An outer-sphere reaction may still provide a path of lower energy.

A reaction is most conveniently assigned to the inner-sphere category if the bridging ligand can be detected in the coordination sphere of the product of the labile reactant at higher than equilibrium levels. This requires that it be retained due to an inertness of this product to substitution relative to the rate of the redox reaction. Exemplifying this means of categorization is the classical reaction between the substitution-inert complex, $[Co(NH_3)_5(Cl)]^{2+}$, and substitution-labile $[Cr(H_2O)_6]^{2+}$ in acid solution to yield NH_4^+, substitution-labile $[Co(H_2O)_6]^{2+}$ and substitution-inert $[Cr(H_2O)_5(Cl)]^{2+}$.[12] The capture of the chloride ion in the first coordination sphere of the inert chromium(III) product is definitive of an inner-sphere reaction. When the same reaction is carried out in the presence of radioactive free chloride ion, no radioactivity is found in the chromium(III) product, thus eliminating its incorporation prior or subsequent to electron transfer which identifies the coordinated chloride in the product as originating with the cobalt(III) complex.[12] Other donor functions which have been identified as bridging ligands for cobalt(III)-chromium(II) reactions are the halides, carboxylates, azides, thiocyanates, phosphate, sulfate and hydroxide.[12,13] In contrast, an outer-sphere reaction is decisively dictated if one of the reactants is substitution-inert relative to the rate of electron transfer and contains in its first coordination sphere no ligand capable of bridge formation. A well-characterized example is the outer-sphere reductant, $[Ru(NH_3)_6]^{2+}$.[14]

The investigation of the mercaptide and alkoxide complexes previously described established, through characterization of the chromium(III) products, that the reactions of the species with chromium(II) occur _via_ inner-sphere paths.[10] The reduction of $[Co(en)_2(OOCCH_2O)]^+$ was concluded to occur _via_ a bridging reaction utilizing the alkoxide oxygen from kinetic comparisons. It is directly comparable, therefore, to the reduction of $[Co(en)_2(OOCCH_2S)]^+$ which proceeded _via_ a mercaptide bridged path as established by product characterization. The results clearly established a reactivity toward chromium(II) for the sulfur complex which is $\sim 10^3$ times greater than for its oxygen analogue.

While the previous research established that the coordinated mercaptide exerted a substantial increase in reactivity for oxidation-reduction, several important questions remained unanswered. The various factors which might possibly contribute to this enhanced reactivity remained unevaluated though recognized. In particular, the relative influence of steric vs electronic factors could not be determined. It seemed desirable to evaluate these influences in complexes as similar as possible in order to minimize any effects arising from the contribution of the standard free energy change to the reactivities.[15] Thus, if a greater steric accessibility of the larger sulfur atom were mainly responsible for the observed reactivity pattern in otherwise comparable complexes, it was felt substitution of a methyl group for one of the adjacent methylene protons should decrease the rate reduction of the sulfur complex less than that of the analogous oxygen complex. Further, if the anticipated rate decrease is observed, the possibility would arise of determining the enthalpies and entropies of activation which were not accessible for the mercaptoacetato complex. These should shed further light on the steric and electronic contributions to the reactivity differences. Thus, the complexes $[Co(en)_2(OOCCH(CH_3)S)](ClO_4)$ and $[Co(en)_2(OOCCH(CH_3)O)](ClO_4)$ were prepared in order to further define the influence of coordinated mercaptide.

It was hoped that the above modification in the alkoxide ligand would permit a more definitive characterization of the chromium(III) product as deriving from alkoxide bridging than was possible with the previously investigated analogue. When this was found not to be the case, a complex having a chelate ligand which contained a carboxylate function as the only possible bridging group, $[Co(en)_2(OOCCH_2NH_2)]^{2+}$,[16] was investigated in order to isolate any unique effects arising from chelation relative to those previously established for monodentate carboxylate coordination.[15] Comparison utilizing results with this complex were expected to more rigorously define, and possibly exclude, the participation of carboxylate bridging for the alkoxide-containing complexes.

In spite of its demonstrated biological importance the redox influence of coordinated thioether functions remains poorly understood. The first kinetic study directly involving this mode of coordination in simple systems suggests that the effect of thioether donor functions as non-bridging ligands in an inner-sphere reaction is to enhance reactivity.[17] Earlier rate studies of complexes such as $[Co(NH_3)_5(OOCCH_2SCH_2C_6H_5)]$ suggested that a pendant thioether enhanced electron transfer rates above that observed with the coordinated carboxylate alone, presumably via chelation of the reductant.[18] In anticipation of this possibility and in collaboration with concurrent research[19] the complex $[Co(en)_2(OOCCH_2SCH_3)]^{2+}$ was prepared and studied. Whatever the mechanistic pathway taken, it was expected that the similarity of this complex to the previously studied mercaptide precursor should provide a better understanding of the influence of coordination by a thioether donor.

Thus, the objectives of this thesis include (1) evaluation of the steric and electronic factors responsible for the increased reactivity of mercaptide complexes relative to their oxygen analogues, (2) further comparison of these influences within the respective alkoxide and mercaptide classes of complexes, (3) definition of the role played by carboxylate incorporated in chelate system as opposed to the monodentate carboxylate function and (4) an investigation into the accessible aspects of thioether coordination with the additional complex made available by this research. Further, the behavior of the chromium(III) complexes uniquely produced by reactions originally investigated for their relevance to oxidation-reduction chemistry should contribute to a better understanding of the substitutional characteristics of these ligands.

EXPERIMENTAL

Materials

Reagents.--Common chemicals were of reagent grade and were used without further purification unless otherwise specified.

Water.--Distilled water used in kinetic experiments and in preparation of various stock reagent solutions was obtained by the distillation of deionized water from alkaline permanganate solution using an all-glass distilling assembly and stored in poly-stoppered, glass bottles.

Nitrogen.--For deaerating solutions of air-sensitive materials, line nitrogen was passed through two successive scrubbing towers containing Cr(II) solutions which were prepared by reducing 0.1 M chromium(III) ion in 0.4 M perchloric acid in the towers with a bed of amalgamated zinc. To assure the nitrogen was saturated with water, it was then passed through a tower containing redistilled water.

Zinc amalgam.--Twenty mesh granular zinc (Fisher) was activated with 3 M HCl. After several rinsings with distilled water the activated zinc was amalgamated using a solution of tetrachloromercurate(II) ion in 1 M HCl for ten seconds. After several washings with distilled water the amalgam was dried under a stream of dry nitrogen.

Lithium perchlorate.--Reagent grade lithium perchlorate was used throughout to maintain constant ionic strength. Purity was checked by passing a prepared solution through an ion exchange column in the acid form and titrating the collected solution with 0.1 M sodium hydroxide to a phenophthalein end point.

Chromium(II) ion.--Reagent grade chromium(III) perchlorate (G. F. Smith) was used to prepare stock solutions ranging in concentration from 0.050 M to 0.25 M. Aliquots of the stock solutions were diluted to concentrations ranging from approximately 4×10^{-4} M to 2×10^{-1} M in solutions varying in acidity from 1×10^{-4} M to 1 M. Reduction to chromium(II) was accomplished using zinc amalgam.

Chloropentaamminecobalt(III) chloride.--This compound was kindly made by Mr. Peter F. Eisenhardt, who used a standard procedure for its preparation.[20] The compound exhibited a molar absorbtivity of 49.9 at 534 nm in excellent agreement with the values of 50.2 - 51.0 previously reported.[21,22]

Mercaptoacetatobis(ethylenediamine)cobalt(III) perchlorate.--This compound was generously provided by Dr. Robert H. Lane, by whom it was first prepared and characterized.[9] The sample provided exhibited the following spectral characterization: [$\lambda(\epsilon)$: 518(152), 282(11,700)].

2,2'-Dithiodipropionic acid.--2-mercaptopropionic acid (Aldrich Chemical Co., reagent grade) was converted to the disulfide by a modification of the method of Fredga and Bjorn[23] which appears to be general for preparation of simple disulfides from the corresponding mercaptans.[8d,e,f,24] One millimole of the mercaptan was slowly added to a solution of one millimole iron(III) perchlorate dissolved in 200 ml of water. After addition the solution was allowed to stir for one hour, several drops of concentrated sulfuric acid was added, and the reaction mixture extracted with three 50 ml portions of diethyl ether. The combined ethereal extracts were evaporated to dryness under a stream of nitrogen. The resultant white solid exhibited a melting point of 113°C uncorrected (lit. 114° - 5.0°C)[23] and was used without further purification.

Preparation of Complexes

2-Mercaptopropionatobis(ethylenediamine)cobalt(III) Perchlorate-- $[Co(en)_2(OOCCH(CH_3)S)]ClO_4$

Preparation of this compound paralleled the method used in preparation of the mercaptoacetatobis(ethylenediamine)cobalt(III) complex previously reported.[9] Ten grams (.028 mole) of $Co(ClO_4)_2 \cdot 6H_2O$ (G. F. Smith) was dissolved in 30 ml of H_2O in a 100 ml three-neck flask fitted with rubber septum stopper, nitrogen inlet and outlet, and magnetic stirrer. After deaeration for thirty minutes, 3.6 ml (.057 mole) of 98-100 per cent ethylenediamine (Baker) was added by syringe. After another thirty minutes' deaeration time, 2.85 g of solid 2,2'-dithiodipropionic acid was added by rapid removal and replacement of the nitrogen outlet tube. Within five minutes the solid had dissolved and the solution color changed slightly to a brown color. After thirty minutes under nitrogen the solution was transferred to a 150 ml beaker, and evaporated with stirring on a hot plate at 100°C under a gentle stream of nitrogen until the volume was approximately 20 ml then allowed to cool to ambient temperature. The resultant foamy brown mass was filtered and washed with 5 ml of hot water. Recrystallization was effected by dissolving the collected solid in 100 ml of hot (90°C) water, filtering, and cooling in an ice-acetone slush. Light purple needles separated on cooling. The product was recrystallized twice more as described, washed with two 10 ml portions of absolute ethanol and one 10 ml portion absolute diethyl ether, then dried in vacuo over $CaSO_4$ for twelve hours. Yield = 2.5 g. Anal. Calcd. for $[Co(NH_2CH_2CH_2NH_2)_2(OOCCH(CH_3)S)]ClO_4$: C, 21.97; H, 5.27; N, 14.64; S, 8.36; Co, 15.40. Found: C, 21.75; H, 5.34; N, 14.61; S, 8.32; Co, 15.15.

Lactatobis(ethylenediamine)cobalt(III) Perchlorate--$[Co(en)_2(OOCCH(CH_3)O)]ClO_4$

Eighteen grams (.05 mole) of $Co(ClO_4)_2 \cdot 6H_2O$ (G. F. Smith) was dissolved in 125 ml of water in 250 ml Erlenmeyer flask fitted with a two-hole rubber stopper with glass tubing of appropriate lengths. Six grams (.10 mole) ethylenediamine (Baker) was added with stirring, then air was drawn through the solution for twelve hours. To this solution was added a solution of 5.05 g (.05 mole) 70% aqueous lactic acid (Baker) and 2.00 g (.05 mole) NaOH pellets (Fisher) in 20 ml water. The combined solutions were transferred to a 250 ml beaker and evaporated under a gentle stream of nitrogen with stirring on a hot plate at 100°C until the volume was approximately 100 ml (ca. 40 min). It was cooled to ambient temperature and the solids present were filtered and washed with

10 ml water. The combined filtrate and washing was returned to the hot plate and evaporated as before to a volume of 50 ml, then cooled to ambient temperature. The resulting solid was filtered, washed with 5 ml of water, 15 ml of absolute ethanol, and 15 ml of absolute diethyl ether and dried in vacuo for ten hours over $CaSO_4$. Yield = 4.75 g. Anal. Calcd. for $[Co(NH_2CH_2CH_2NH_2)_2(OOCCH(CH_3)O)]ClO_4$: C, 22.90; H, 5.52; N, 15.27; Co, 16.11. Found: C, 22.86; H, 5.52; N, 15.14; Co, 15.82.

2-Methylthioacetatobis(ethylenediamine)cobalt(III) Diperchlorate-- $[Co(en)_2(OOCCH_2SCH_3)](ClO_4)_2$

To a suspension of 1.8 g of $[Co(en)_2(OOCCH_2S)]^+$ in 300 ml of 90% methanol-water mixture was added a large excess (25-fold) of methyl iodide (Baker). The mixture was stirred in a closed, round-bottom flask for twenty-four hours and for three hours was stirred while open to the atmosphere. The light pink solid was collected, washed with two 25 ml portions of absolute ethanol, two 25 ml portions of diethyl ether and dried in vacuo over $CaSO_4$ for twelve hours. The solid was recrystallized by dissolution in minimum amount of hot (90°C) water followed by an addition of solid $NaClO_4$ (~4 g) until precipitation began. After allowing it to cool to ambient temperature, the bright red-orange solid was collected and recrystallized again. Yield = 0.70 g. Anal. Calcd. for $[Co(NH_2CH_2CH_2NH_2)_2(OOCCH_2SCH_3)](ClO_4)_2$: C, 17.40; H, 4.38; N, 11.60; S, 6.64. Found: C, 17.42; H, 4.26; N, 11.64; S, 6.75.

Glycinatobis(ethylenediamine)cobalt(III) Diperchlorate--$[Co(en)_2(OOCCH_2NH_2)](ClO_4)_2$

This compound was prepared by the reaction of silver perchlorate with glycinatobis(ethylenediamine)cobalt(III)dichloride.[16] Twenty grams of trans-$[Co(en)_2Cl_2]Cl$ was suspended in 40 ml of water. To this was added 8.1 g silver oxide (Matheson, Coleman, and Bell) and the suspension was ground in a mortar and pestle periodically for one hour. Silver chloride was removed by filtration and washed with 40 ml of hot (90°C) water. To the combined filtrate and washings was added 6.9 g glycine (Fisher), and then the mixture was evaporated on a steam bath under a stream of nitrogen to a thick syrup. After standing at ambient temperature, the resultant solid was filtered, washed with cold water, recrystallized from hot water, and dried in vacuo over $CaSO_4$ overnight.

A solution of 6.81 g (0.02 mole) of $[Co(en)_2(OOCCH_2NH_2)]Cl_2$ dissolved in 40 ml water was added slowly with stirring to a silver perchlorate solution prepared by adding 2.36 g (0.0085 mole) silver carbonate (Mallinkrodt) to 10 ml of 2 M perchlorate acid. Silver chloride was removed by filtration and the filtrate was reduced on a rotary evaporator at 45°C to a thick syrup. After several days' standing at ambient temperature the resultant solid mass was filtered and air dried using aspirator suction for 2 days. The solid was dried in vacuo over $CaSO_4$ for twenty-four hours. Yield = 5.0 g. Anal. Calcd. for $[Co(NH_2CH_2CH_2NH_2)_2(OOCCH_2NH_2)](ClO_4)_2$: C, 15.94; H, 4.43; N, 15.49; Co, 13.04. Found: C, 16.13; H, 4.52; N, 15.52; Co, 13.25.

Chromium(III) Complexes of 2-Mercaptopropionic Acid, Lactic Acid and Glycine

Several aquo-chromium(III) complexes with these ligands were generated in solution by the reduction of the cobalt(III) complexes with chromium(II). Some of the complexes so produced underwent further substitutional changes, the products of which were separated according to charge type by ion exchange chromatography and further characterized by their ultraviolet and visible spectrum and by chromium analyses. Synthesis and isolation of the complexes was not a primary objective; therefore, discussion of them is deferred to the section on Results.

Analyses

Chromium(III).--Determination of chromium(III) was accomplished spectrally by alkaline peroxide oxidation to chromate(VI) ion which was monitored at 373 nm ($\epsilon = 4{,}815 \pm 15$).[25] To an aliquot of the chromium(III) complex, 10 ml distilled water, 10 ml 0.20 M NaOH and 3 ml of 30% hydrogen peroxide were added. The oxidation usually was complete overnight. Excess peroxide was deconposed by heating the solution at 60°C using a coiled platinum wire as catalyst. When cool, the solution was diluted to 100 ml and absorbance at 373 nm was observed. Duplicate runs usually were reproducible to within 1%.

Chromium(II).--Periodically aliquots of chromium(II) solutions were reacted in an inert atmosphere with a solution containing a known excess of chloropentaamminecobalt(III) in 0.1 M $HClO_4$. The excess was determined by analyzing speotrally the resultant solution at 534 nm, after subtracting for absorbances due to presence of hexaquocobalt(II) ion (ϵ_{534} = 3.1)[26] and chloropentaaquochromium(III) ion (ϵ_{534} = 5.5).[27]

Cobalt.--The method of Moss and Mellon using 2-2',2"-terpyridine as a complexing agent was used.[28] A sample of complex containing approximately 4 mg cobalt was destroyed using 15 ml liquid fire reagent (7 parts 70% $HClO_4$ - 3 parts 70% HNO_3). The reaction mixture was evaporated just to dryness on a hot plate, with the residue then dissolved in 20 ml distilled water. Addition of 5 ml of 20% ammonium acetate solution brought the pH to about 6 and the solution was then diluted to 100 ml. A 25.0 ml aliquot of the cobalt(II) solution was deaerated using a 50.0 volumetric flask fitted with septum stopper and hypodermic needles for nitrogen inlet and outlet. Ten milliliters of 0.2% terpyridyl solution was injected and volume brought to 50.0 ml by syringe addition of deaerated distilled water. A sample was then transferred to a deaerated septum-stoppered 2 cm cell using syringe techniques and the concentration of the cobalt(II) terpyridyl complex determined spectrally at 505 nm. A molar absorbtivity of 1,386 at 505 nm determined with known cobalt solutions[29] was used rather than the reported value of 1,360.[28]

Elemental analyses.--Analyses for carbon, hydrogen, nitrogen and sulfur were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. Nitrogen analyses were performed by the Kjeldahl method.

Apparatus

It was necessary to exclude the presence of oxygen from reactant solutions used in kinetic studies due to the extreme sensitivity of the chromium(II) species to oxidation in solution. This was accomplished by deaeration of all solutions using three-neck flasks fitted with nitrogen inlet, outlet, and rubber septum for syringe withdrawal of solutions. Times for purging ranged from thirty minutes to one hour. Transfers of deaerated solutions were made using all-glass graduated syringes fitted with stainless steel needles.

For all kinetic studies at least one of the reactants exhibited a characteristic absorbance in the visible and/or near ultraviolet region. Reactions were then monitored optically at the respective absorbances.

Kinetic Studies

Fast reactions (1 msec $< t_{\frac{1}{2}} >$ 15 sec) were monitored using a Durrum-Gibson Stopped-Flow Spectrophotometer equipped with tungsten and deuterium light sources, Kel-F flow system, and an AMINCO 4-8600 external temperature bath. Use of an external circulating pump maintained a constant temperature environment for the drive syringes, mixing jet, and observation chamber.

Thermostatted, deaerated reactant solutions were transferred to the stopped-flow assemble *via* 20 ml reservoir syringes. The drive syringes were filled from the reservoir syringes by a system of externally sealed Kel-F valves. The filled drive syringes were then allowed to equilibrate to the desired temperature (estimated) for five to thirty minutes. A plunger armed by nitrogen pressure (65 psi) and fitted with external, integrated trigger then forced the reactant solutions into the observation chamber via the mixing jet. Mixing and instrument mechanical dead times (2 msec) were, in some instances, comparable to the shortest half-life of the reactions so studied. For these cases it was necessary to allow for the dead time and begin actual reaction study after one or two half-lives had passed.

Data were recorded first on the storage oscilloscope, then reproduced using Type 47, 3000 speed Polaroid Film (B & W) using a Polaroid Land Camera Bank mounted on a Tektronix C-27 Oscilloscope Camera with appropriate bezel attachment. Kinetic data were obtained in the temperature range 15.0°C to 45.0°C as necessary.

No special precautions were taken to exclude oxygen other than flushing the flow system with several volumes of the deaerated reactant solutions. This technique was found to be sufficient for solutions of chromium(II) ion concentration greater than 4×10^{-4} M as evidenced by reproducibility of the observed rate constant (within 10%) for the Cr(II)-$[Co(en)_2(OOCCH(CH_3)S)]^+$ reaction when the concentration of Cr(II) prior to mixing was 4.3×10^{-4} M. Below this level partial consumption of the reductant occurred.

Slow reactions were followed by use of Cary 14 Recording Spectrophotometer fitted with constant temperature cell housing. Temperature was maintained with an AMINCO 4-8605 constant temperature bath equipped with an external circulating pump. Reaction solutions were again deaerated and thermostatted before mixing.

Some of the reactions followed on the Cary 14 utilized a glass mixing apparatus described pictorially elsewhere.[14b] Essentially the apparatus consisted of two reservoirs placed so as to form a "V" with an aperture for a rubber septum stopper to introduce the respective reactant solution and with provision for maintaining an inert atmosphere. At the apex of and perpendicular to the "V" was delivery tube with pressure equalizing arm, fitted with ground glass joint appropriate for the quartz cells. Tilting the apparatus, and shaking to mix, then draining into the cell effected reaction. Initial data were obtainable within ten seconds of mixing.

Spectrophotometry

Visible and near-ultraviolet spectra were obtained with a Cary Model 14 Recording Spectrophotometer. Sample solutions and baselines of pure solvent were run against air as the reference. Quartz cells of 0.10, 1.00, 2.00, 5.00, and 10.0 cm path lengths were available.

Infrared spectra were obtained from 4,000 to 625 cm^{-1} with a Perkin-Elmer Model 337 recording infrared spectrophotometer. All samples were run as KBr pellets.

Proton Magnetic Resonance Spectra

PMR spectra were obtained with a Varian A-60A Analytical NMR Spectrophotometer with a magnet temperature of 37°C. In order to reach a concentration of complex large enough to obtain meaningful spectra for the 2-mercaptopropionic acid complex, it was necessary to convert the complex from the perchlorate to the chloride salt. This was accomplished by the reaction of 0.100 mmole of complex with 0.095 mmole of tetraphenylarsonium chloride (G. F. Smith) in a minimum volume of water. The resulting tetraphenylarsonium perchlorate formed was removed by filtration, and the filtrate evaporated to dryness on a rotary evaporator and dried in a vacuum desiccator overnight.

Spectra of saturated solutions of the chloride in deuterium oxide (99.5%, Matheson, Coleman, and Bell) were obtained with TMS used as an external standard. Solutions were made acidic (pD = 1) with trifluoroacetic anhydride (Aldrich).

The solubility of the lactic acid and methylthioacetic acid complexes posed no such problem and spectra were obtained using the perchlorate salt.

Ion Exchange Studies

All ion exchange separations were carried out using Biorad AG 50W-X2, 200-400 mesh (purified standard Dowex resin of the same designation), analytical grade cation exchange resin. The resin was converted to either the sodium or lithium form from the hydrogen form by soaking and washing the resin in a solution of 1 M in NaOH--$NaClO_4$ or LiOH--$LiClO_4$, then rinsing with distilled water until the eluent was neutral to Hydrion paper.

Because of the fine mesh of the resin, nitrogen pressure (15 psi) was used to increase the flow rate from 1-2 ml/min to 6-7 ml/min. Separation of bands was adequate under conditions of the latter flow rate. Elution characteristics for several ions of interest are given in Table I (p. 27).

Treatment of Kinetic Data

For all the oxidation-reduction reactions studied it was determined that the reactions were first order in both oxidant and reductant over the ranges considered. The stoichiometry was established to be one mole of oxidant consumed per mole of reductant, vide infra. The differential rate law then for reactions first order in each species may be expressed as follows:

$$\frac{-d[R]}{dt} = \frac{-d[O]}{dt} = k_{obs}[R][O] \qquad (1)$$

where $[R]$ and $[O]$ are the respective concentrations of reductant and oxidant and k_{obs} is the rate constant observed at a given acidity. In some cases the rate was also a function of acidity as well. Determination of acid dependencies will be discussed with the specific reactions involved.

Integration of the differential equation above yields, when the reductant is in excess,

$$\log \left(\frac{[R]_\circ - x}{[O]_\circ - x} \right) = \frac{([R]_\circ - [O]_\circ)kt}{2.303} + \log \left(\frac{[R]_\circ}{[O]_\circ} \right) \qquad (2)$$

where the subscript ($_\circ$) represents initial concentrations and x represents the concentration consumed at time, t.

The use of Beer's Law ($A = \epsilon bC$, where the terms are absorbance, molar extinction coefficient, cell path length in cm, and concentration in moles per liter, respectively) allows the expression of equation (2) in terms of experimentally observable parameters. If one or more of the reactants and/or products has a characteristic absorbance at the wave length monitored, equation (2) may be expressed as

$$\log \frac{A_t + \left(\frac{[R]_o}{[O]_o} - 1 \right) A_o - \left(\frac{[R]_o}{[O]_o} \right) A_\infty}{A_t - A_\infty} =$$

$$\frac{([R]_o - [O]_o)kt}{2.303} + \log \left(\frac{[R]_o}{[O]_o} \right) \qquad (3)$$

where A is the absorbance observed at the respective times ($_o$, t, and $_\infty$). A plot of the left side of equation (3) vs time allows an observed rate constant to be determined (i.e., slope = $\frac{([R]_o - [O]_o)k}{2.303}$).

Wherever feasible a large excess of reductant ($[R]_o > 10[O]_o$) was used. Under this condition equation (3) may then be reduced to the form

$$\log (A_t - A_\infty) = -\frac{k_{obs}t}{2.303} + \log (A_o - A_\infty) \qquad (4)$$

where $k_{obs} = [R]_o k$. In this case a plot of $\log (A_t - A_\infty)$ vs t allows an observed rate constant to be obtained. Use of the average value of $[R]_o$ reduces the inherent error in the approximation leading to equation (4). The derivation of equations (3) and (4) can be found elsewhere.[10]

For the cases where the forward and reverse rate constants were to be evaluated for an equilibrium reaction of the type

$$Z + H^+ \underset{k_r}{\overset{k_f}{\rightleftharpoons}} P$$

where $[P]_o = 0$, $[Z]_o = Z$, and hydrogen ion was present in large excess, equation (4) may be utilized by replacing A_∞ with A_{eq}. Thus

$$\log\ (A_t - A_{eq}) = -\frac{k_{obs}t}{2.303} + \log\ (A_o - A_{eq}) \qquad (5)$$

where $k_{obs} = k_f + k_r$. The forward and reverse rate constants were thus derived from

$$k_f = \frac{k_{obs}}{1 + (1/K_{eq}[H^+])}, \quad k_r = \frac{k_{obs}}{1 + K_{eq}[H^+]}, \quad K_{eq} = \frac{[P_{eq}]}{[Z_{eq}][H^+]}$$

Elucidation of this method is discussed elsewhere.[30,31]

Evaluation of Activation Parameters

Consider the simple bimolecular reaction

$$R + O \overset{K^*}{\rightleftarrows} (RO)^* \overset{k^*}{\rightleftarrows} \text{Products}$$

where species R and O form the activated complex $(RO)^*$ which then may proceed to products. Following methods previously outlined,[32] K^* can be treated as an equilibrium constant and the reaction rate expressed as

$$\frac{-d[R]}{dt} = k_p[R][O] = k^*K^*[R][O] = \frac{kT}{h}K^*[R][O] \qquad (6)$$

$$\text{and} \quad k_p = (\frac{kT}{h})K^* \qquad (7)$$

where k_p is the observed rate constant, k is Boltzmann's constant, h is Planck's constant, and T is the absolute temperature. Treatment of K* as an equilibrium constant allows the expression

$$\Delta G^* = -RT \ln K^* \tag{8}$$

to be used. Then

$$k_p = \frac{kT}{h} e^{-\Delta G^*/RT} = \frac{kT}{h} e^{\Delta S^*/R} e^{-\Delta H^*/RT} \tag{9}$$

Equation (9) may then be converted into the form of a linear equation to yield

$$\log \left(\frac{k_p}{T}\right) = \log \left(\frac{k}{h}\right) + \frac{\Delta S^*}{2.3R} - \frac{\Delta H^*}{2.3RT} \tag{10}$$

A plot of $\log \left(\frac{k_p}{T}\right)$ vs $\frac{1}{T}$ then yields a value for ΔH^* from the slope, m:

$$\Delta H^* = -2.3R(m) \tag{11}$$

The entropy of activation can be obtained from the y-intercept, b, by using equation (12).

$$\Delta S^* = b - \log \left(\frac{k}{h}\right) 2.3R \tag{12}$$

RESULTS

Characterization of Complexes

Spectral and ion exchange properties upon which the characterization of all complexes are partially based are summarized in Tables I, II and III. Proton magnetic resonance data for the methyl, methylene and methinyl protons of interest are listed in Table IV.

2-Mercaptopropionatobis(ethylenediaminc)cobalt(III) Perchlorate--$[Co(en)_2(OOCCH(CH_3)S)]ClO_4$

Characterization of this complex was accomplished by elemental analysis, infrared, visible, ultraviolet, and proton magnetic resonance spectroscopy, ion exchange chromotography, acidity studies and reaction patterns both independently and in comparison with the previously reported mercaptoacetato complex.[10] The basis for the formulation of the complex as written, bound through carboxylate oxygen and mercaptide sulfur, will now be summarized.

Elemental analyses for carbon, hydrogen, nitrogen, sulfur and cobalt as previously reported in the Experimental section were in good agreement with the calculated percentages. The infrared spectrum of the complex exhibited no absorption in the 2,500 cm^{-1} area which substantiates the sulfur being deprotonated in the complex as a solid. Intense absorption at 1,630 cm^{-1} and 1,340 cm^{-1}

TABLE I

Elution Characteristics of Some Cobalt(III) and Chromium(III) Species[a]

Species	Eluent[b]	V_1(ml)[c,e]	V_2(ml)[d,e]
cis-$[Co(en)_2(Cl)_2]^+$	1	65	40
$[Co(en)_2(OOCCH(CH_3)S)]^+$	1	60	30
	2	35	20
$[Co(en)_2(OOCCH(CH_3)O)]^+$	1	55	30
$[Co(en)_2(OOCCH(CH_3)OH)]^{2+}$	2	100	50
$[Co(en)_2(OOCCH_2SCH_3)]^{2+}$	1	325	130
$[Co(en)_2(OOCCH_2NH_2)]^{2+}$	1	420	140
	2	125	70
$[Co(H_2O)_6]^{2+}$	1	210	100
	2	90	40
$[Co(en)_3]^{3+}$	1	1000	--
	2	600	--
$[Cr(H_2O)_4(OOCCH(CH_3)S)]^+$	1	45	25
$[Cr(H_2O)_4(OOCCH(CH_3)O)]^+$	1	50	25
$[Cr(H_2O)_5(OOCCH(CH_3)SH)]^{2+}$	2	90	40
$[Cr(H_2O)_5(OOCCH(CH_3)OH)]^{2+}$	2	85	40
$[Cr(H_2O)_5(OOCCH_2SCH_3)]^{2+}$	1	115	50
$[Cr(H_2O)_5(OOCCH_2NH_3)]^{3+}$	2	550	200
$[Cr(H_2O)_6]^{3+}$	1	230	100
	2	110	45

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[a] 30 x 1.25 cm column in Na^+ form. 0.2 mmole used of each ion. [b] Eluents: (1) 1.0 M $NaClO_4$; (2) 0.10 M $HClO_4$--2.0 M $NaClO_4$. [c] Volume eluent passed before band starts to elute. [d] Volume eluent passed for elution of band. [e] Approximate volumes. Duplicate runs varied up to 15%.

Spectral Parameters of Some Cobalt(III) Species

Species	λ(ϵ)	λ(ϵ)	λ(ϵ)	pH	Ref.
$[Co(en)_2(OOCCH(CH_3)S)]^+$	517(153)	360(350)	282(12,350)	0-7	a
$[Co(en)_2(OOCCH(CH_3)O)]^+$	517(139)	360(150)	--	7	a
$[Co(en)_2(OOCCH(CH_3)OH)]^{2+}$	499(113)	349(123)	--	1	a
$[Co(en)_2(OOCCH_2SCH_3)]^{2+}$	499(168)	360(250)	280(7,300)	1-6	a
$[Co(en)_2(OOCCH_2NH_2)]^{2+}$	487(98)	346(106)	--	0-7	a
$[Co(en)_2(OOCCH_2NH_2)]^{2+}$	487(98)	346(107)	--	0-7	2
$[Co(en)_2(H_2O)(OOCCH(CH_3)OH)]^{2+}$	498(~100)	360(~80)	--	1	a,b
$[Co(en)_2(OOCCH_2S)]^+$	518(152)	--	282(12,600)	0-7	10
$[Co(en)_2(OOCCH_2O)]^+$	518(132)	360(140)	--	7	10
$[Co(en)_2(OOCCH_2OH)]^{2+}$	499(113)	348(122)	--	1	10
$[Co(en)_2(H_2O)(OOCCH_2OH)]^{2+}$	498(~100)	360(~80)	--	1	10
$[Co(en)_2(OCH_2CH_2S)]^+$	524(139)	--	283(12,600)	7	10
$[Co(en)_2(NH_2CH_2CH_2S)]^{2+}$	482(138)	370(283)	282(13,200)	0-7	19
$[Co(NH_3)_5(OOCCH(CH_3)OH)]^{2+}$	503(73)	350(62.1)	--	7	9
cis-$[Co(en)_2(OH)(OOCCH_3)]^+$	512(101)	365(85)	--	?	c
cis-$[Co(en)_2(H_2O)(OOCCH_3)]^{2+}$	498(100)	360(77.5)	--	?	c
cis-$[Co(en)_2(Cl)(NH_2CH_2COO)]^+$	525(80)	365(83)	--	?	2

[a] This work. [b] From hydrolysis of $[Co(en)_2(OOCCH(CH_3)OH)]^{2+}$. [c] V. Carunchio, G. Illuminati, and G. Ortaggi, Inorg. Chem., 6, 2168 (1967).

TABLE III

Spectral Parameters of Some Chromium(III) Species

Species	$\lambda(\epsilon)$	$\lambda(\epsilon)$	$\lambda(\epsilon)$	pH	Ref.
$[Cr(H_2O)_4(OOCCH(CH_3)S)]^+$	545(71.2)	440(52.2)	265(5,050)	1-2	[a]
$[Cr(H_2O)_5(OOCCH(CH_3)SH)]^{2+}$	568(25.0)	411(24.3)	--	1-2	[a]
$[Cr(H_2O)_4(OOCCH(CH_3)O)]^+$	548(31.0)	437(38.0)	--	52.8	[a]
$[Cr(H_2O)_4(OOCCH(CH_3)O)]^+$	570(40.1)	411(45.0)	--	?	35
$[Cr(H_2O)_5(OOCCH(CH_3)OH)]^{2+}$	568(26.8)	413(33.2)	--	1	[a]
$[Cr(H_2O)_5(OOCCH(CH_3)OH)]^{2+}$	563(25.7)	409(31.2)	--	?	41
$[Cr(H_2O)_5(OOCCH_2SCH_3)]^{2+}$	567(26.7)	412(25.9)	--	1-2	[a]
$[Cr(H_2O)_5(OOCCH_2SH)]^{2+}$	568(26.0)	411(25.1)	--	1-2	10
$[Cr(H_2O)_4(OOCCH_2NH_2)]^{2+}$	555(38.0)	420(41.0)	--	4.5	[a]
$[Cr(H_2O)_5(OOCCH_2NH_3)]^{3+}$	572(22.0)	412(23.0)	--	3	[a]
$[Cr(H_2O)_4(OOCCH_2S)]^+$	548(68.3)	437(53.4)	264(5,070)	1-2	10
$[Cr(H_2O)_4(OOCCH_2O)]^+$	548(32.5)	436(38.5)	--	2.8	10
$[Cr(H_2O)_5(OOCCH_2OH)]^{2+}$	568(24.5)	411(30.5)	--	1	10
$[Cr(H_2O)_5(SH)]^{2+}$	574(27)	434(43)	259(∼7,000)	0-2	34
$[Cr(H_2O)_5(OOCCH_3)]^{2+}$	570(24.4)	410(22.2)	--	7	25
$[Cr(H_2O)_6]^{3+}$	574(13.4)	408(15.6)	--	7	43

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[a] This work.

TABLE IV

PMR of Various Protons Adjacent to Chalcogens

Species	Medium	Methinyl[a] Proton	Methyl[a] Protons	Methylene[a] Protons	Ref.
$HOOCCH(CH_3)SH$	$CDCl_3$	3.58	1.56	--	b
$DOOCCH(CH_3)SD$	D_2O	3.65	1.48	--	c
$NaOOCCH(CH_3)SD$	D_2O	3.45	1.35	--	c
$[Co(en)_2(OOCCH(CH_3)S)]^+$	D_2O	3.51	1.32	--	c
$[Co(en)_2(OOCCH(CH_3)S)]^+$	D_2O-CF_3COOD	3.51	1.32	--	c
$NaOOCCH(CH_3)OD$	D_2O	4.09	1.30	--	d
$[Co(en)_2(OOCCH(CH_3)O)]^+$	D_2O	3.92	1.25	--	c
$[Co(en)_2(OOCCH(CH_3)OD)]^{2+}$	D_2O-CF_3COOD	4.36	1.32	--	c
$CH_3SCH_2CH_2COOCH_3$	D_2O	--	2.08	2.55	d
$CH_2(S\underset{A}{CH_2}COOH)_2$	CF_3COOD	--	--	A=3.62	d
$[Co(en)_2(OOCCH_2SCH_3)]^{2+}$	D_2O	--	2.38	3.75	c
$[Co(en)_2(OOCCH_2SCH_3)]^{2+}$	D_2O-CF_3COOD	--	2.38	3.75	c
D_2NCH_2COOD	D_2O	--	--	3.58	d
$[Co(en)_2(OOCCH_2NH_2)]^{2+}$	D_2O	--	--	3.58	e
$NaOOCCH_2SD$	D_2O	--	--	3.51	d
$HOOCCH_2SH$	$CDCl_3$	--	--	3.31	d
$[Co(en)_2(OOCCH_2S)]^+$	D_2O	--	--	3.10	10
$[Co(en)_2(OOCCH_2S)]^+$	D_2O-CF_3COOD	--	--	3.10	10
$NaOOCCH_2OD$	D_2O	--	--	3.99	d
$DOOCCH_2OD$	D_2O	--	--	4.29	d
$[Co(en)_2(OOCCH_2O)]^+$	D_2O	--	--	3.90	10
$[Co(en)_2(OOCCH_2OD)]^{2+}$	D_2O-CF_3COOD	--	--	4.26	10
$CH_3SCH_2CH(ND_2)COOD$	D_2O	4.51	2.22	3.27	d
$[Co(en)_2(OOCCH(CH_2SCH_3)NH_2)]^{2+}$	D_2O	3.60	2.22	3.08	39

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[a] Downfield from TMS (in ppm). [b] Varian Associates Catalog, Vol. II. [c] This work. [d] Sadtler Tables. [e] D. H. Williams and D. H. Busch, J. Amer. Chem. Soc., 87, 4644 (1965).

indicate the presence of coordinated carboxylate.[16,33] These data are consistent with the ion exchange studies which indicated a unipositive ion (Table I).

Spectral parameters in the visible and near-ultraviolet for the compound are as follows: [$\lambda(\epsilon)$: 517(152 ± 2), 360(340 ± 20), 282($1.23 \pm 0.02 \times 10^4$)]. The error associated with the molar absorptivity at 360 nm corresponding to the ${}^1T_2 \leftarrow {}^1A_1$ d-d transition is due to its super position on the tail of the intense band at 282 nm. This contributes to the rather high value for the molar absorptivity at 360 nm with intensity borrowing from the higher energy peak also appearing important. It was necessary to use the ultraviolet rather than the visible source because the slit width with the former allowed for better resolution at the 360 nm setting to define the shoulder clearly.

The near-ultraviolet peak is assigned to sulfur-to-metal charge transfer due to its large molar absorptivity and the appearance of similar peaks (±2 nm) in the spectra of the 2-mercaptoacetato, 2-mercaptoethanolato and 2-mercaptoethylamine complexes. Similar peaks are absent in the spectra of the oxygen analogues. A fourth absorbance with maximum near 220 nm and molar absorptivity of 19,000 ± 2,000 was noticed for the thiolactato, lactato, mercaptoacetato, glycolato and glycinato species, but reproducibility is less than desirable. It is tempting to assign this transition to carboxylate oxygen-to-metal charge transfer which would then correlate the lower energy sulfur-to-metal charge transfer with the greater ease of oxidation of sulfur relative to oxygen.

As for the mercaptoacetato complex,[10] no change in visible or near-ultraviolet spectral parameters over the pH range 0-7 lead to the conclusion that the thiclactato complex is not detectably basic under the conditions studied. Kinetic data support this observation, vide infra. The lack of basicity in this range is comparable to the results observed for the mercaptoacetato cobalt complex[10] and thiolochromium complex.[34,35]

Proton magnetic resonance spectra of several cobalt(III)-chalcoganide complexes previously have shown that the resonance of the methylene protons contiguous to the coordinated chalcogenide is shifted upfield by 0.2 - o.7 ppm from the neutral free ligands and that deuteronation of coordinated alkoxide shifts the methylene resonance to near that of the free ligand.[10,19,36] It has also been demonstrated that the resonance of methylene protons adjacent to coordinated sulfur remains shifted equally upfield from the free ligand in both neutral and acidic media.[10,19]

From these results it was expected that the methinyl proton on the propionate skeleton would exhibit similar behavior. The resonance of the methinyl proton adjacent to coordinated sulfur in the 2-mercaptopropionate skeleton is shifted upfield from the neutral free ligand resonance but by the smallest amount yet observed, 0.14 ppm. Such a small shift seems inadequate to diagnose sulfur coordination except in combination with other supportive data such as that presented here. The methyl resonance is similarly shifted upfield by only a small amount, 0.16 ppm. The lack of response in the methyl resonance to acidification supports the contention that sulfur is not protonated over the acid range studied. The reactivity patterns and product studies described below provide further confirmation of the formulation of the complex as described.

Lactatobis(ethylenediamine)cobalt(III) Perchlorate--$[Co(en)_2(OOCCH(CH_3)O)]ClO_4$

Similar techniques were employed for the characterization of this complex. Elemental analyses for carbon, hydrogen, nitrogen and cobalt were in good agreement with the calculated values for the complex as a unipositive ion coordinated through both carboxylate and alkoxide oxygen atoms (Experimental section). Further, the complex eluted as a +1 ion with neutral eluent and as a +2 ion with an eluent of pH = 1 using the previously described ion exchange methods (Table I).

Infrared spectral data confirm the presence of coordinated carboxylate which exhibits maxima at 1,630 cm^{-1} and 1,350 cm^{-1}. Determination of the presence or absence of coordinated alkoxide by examination of the O-H stretching region was rendered impossible due to broad N-H and C-H stretching mode absorption originating from the ethylenediamine ligands in the 3,500 cm^{-1} and 3,000 cm^{-1} region.

Spectral parameters in the visible and near-ultraviolet regions are as follows: $[\lambda(\epsilon)$: 517(138, 360(153) in neutral water and 499(113), 349(123) in 0.10 M $HClO_4]$. An absorption near 220 nm with unreliable reproducibility in molar absorptivity was also present.

Determination of the K_a of the complex was necessary due to its inclusion in the rate expression at low pH, vide infra. A value was obtained using three methods of determination which gave good agreement. A pK_a of 3.36 at 1.0 M ionic strength ($LiClO_4$) was obtained by spectral methods.[25] Direct electrometric titration with 0.100 N HCl of one millimole of complex in 100 ml of water gave pK_a = 3.33. A titration with 0.100 N NaOH of one millimole dissolved in 25.0 ml 0.100 N HCl (providing a known excess) yielded pK_a = 3.43 (μ = 0.10 M). A value of 3.37 ± 0.06 was adopted as the pK_a of the complex. It can be seen that there is little, if any, variation with ionic strength as has been found elsewhere.[37] The value of 3.37 is in reasonable comparison with those for the analogous glycollato complex (pK_a = 3.3 ± 0.3) and the 2-aminoethanol complex (pK_a = 3.59).[37] The $[Co(en)_2(OOCCH(CH_3)\text{-}OH)]^{2+}$ ion is more acidic by a factor of $10^{2.7}$ and $10^{2.2}$ over the corresponding cis-diaquo and $[Co(NH_3)_5(HOCH_3)]^{2+}$ complexes with pK_a values of 6.1 and 5.58, respectively.[38,35]

The pmr spectrum of this complex reveals a resonance for the methyl group adjacent to alkoxide oxygen which is only slightly shifted relative to the free ligand monoanion in both neutral and acidic media (Table IV). In contrast, the methinyl proton resonance is shifted upfield by 0.17 ppm from the free ligand monoanion. The comparisons evident in Table IV suggest that the shift from the free neutral ligand will be comparable to that observed for the glycollate complex. Together with the observation that deuteronation effects a 0.44 ppm shift downfield compared to a 0.36 ppm shift for the glycollate complex, this appears to validate the resonance shift criterion for alkoxide coordination. The diminished sensitivity of the 2-mercaptopropionate methinyl resonance to mercaptide coordination is not understood but may arise from steric effects.

The pmr spectra, the acidity of the complex, failure to incorporate water on recrystallization and the striking similarity in the visible spectra (both in acidic and neutral media) to the analogous glycollato complex previously characterized and reported[10] provide evidence that the alcohol function is coordinated to the metal center in solution. Reactivity patterns and product studies described below are consistent with this conclusion. Further, prolonged exposure of the complex to 0.10 M $HClO_4$ effects a first-order reaction ($k = 1.9 \times 10^{-7}$ sec^{-1}) to what is assumed to be *cis*-$[Co(en)_2(OH_2)(OOCCH(CH_3)OH)]^{2+}$ on the basis of spectral comparison to the *cis*-acetato-aquo and *cis*-glycollato-aquo analogues (Table II).

2-Methylthioacetatobis(ethylenediamine)cobalt(III) Perchlorate--$[Co(en)_2(OOCCH_2SCH_3)](ClO_4)_2$

This compound was characterized utilizing the methods employed for the previous compounds. Elemental analyses for carbon, hydrogen, nitrogen and sulfur were found to be in good agreement with the calculated values (Experimental section). The finding that analyses for hydrogen and sulfur were very slightly lower and higher, respectively, than the calculated values weighs heavily in favor of coordination through carboxylate oxygen and thioether sulfur since the principal probable impurity, that with water coordinated in place of the thioether function, would reverse the deviations. Ion exchange characteristics for the complex were that of a +2 ion (Table I).

Infrared spectral data confirm the presence of coordinated carboxylate *via* strong absorptions at 1,630 cm^{-1} and 1,350 cm^{-1}, which are characteristic of this mode of coordination.[16,33] The definition of sharp absorbances at 3,470 cm^{-1} and 3,400 cm^{-1} characteristic of N-H stretching modes argues against presence of water in the solid since presence of the latter usually obscures the N-H stretches.[33]

Spectral parameters in the visible and near-ultraviolet for the compound are as follows: [$\lambda(\epsilon)$: 499(168), 360(250), 280 (7,300)]. As previously noted for the 2-mercaptopropionatocobalt-(III) complex, the absorption at 280 nm is taken empirically to be characteristic of metal-sulfur coordination. This transition energy is attributable to alternative formulation only with excessive difficulty. In the pH range 1-6 there was no change in the spectral observations as would be expected for a weakly basic trivalent sulfur atom. For the experimental conditions used in this study the complex was found to be stable in solution for at least four hours, a period much longer than that employed in the kinetic measurements.

The advantage of using as a structural probe, the reaction of a species with a reagent whose reactivity patterns are thoroughly characterized, is demonstrated convincingly in this caso. Reactions of the complex with $[Cr(H_2O)_6]^{2+}$ proceeds in two or three observable steps to yield an isolable carboxylatopentaaquochromium(III) product with the rate of the first step being independent of acid concentration, vide infra. This behavior cannot be reconciled with that expected for the only apparent alternative formulation, $[(en)_2Co(H_2O)(OOCCH_2SCH_3)]^{2+}$, which should be reduced in one step to the carboxylatopentaaquochromium(III) product, or with an inverse acid concentration dependence to yield $[Cr(H_2O)_6]^{3+}$, $[Cr(H_2O)_5(OOCCH_2SCH_3)]^{2+}$ or $[Cr(H_2O)_5(CH_3SCH_2COOH)]^{3+}$. The last complex is, in fact, believed to be the initial product which can convert to the carboxylatopentaaquochromium(III) product in two steps, chelation by carboxylate followed by dechelation at sulfur. However, its genesis by a rapid, acid independent reaction cannot reasonably be attributed to reaction with the alternative complex. Its generation can be rationalized in terms of the formulation presented, vide infra.

The proton magnetic resonance spectrum of the complex appears to provide corroborative support for the thioether function being coordinated. The methyl resonance undergoes a shift of 0.30 ppm downfield, relative to the esterified methylthiopropionic acid, while the methyl resonance for the complex of S-methylcysteine in which the thioether is not coordinated[39] remains unshifted relative to the free ligand value. Further, the methylene resonance is shifted downfield by 0.13 ppm for this complex, relative to a comparable ligand, whereas for the pendant thioether complex, the shift is 0.2 ppm upfield. Thus, if the complex is regarded as being derived from the mercaptoacetate complex by a methyl carbonium ion substitution on coordinated sulfur, the effect on the methyl and methylene resonances are similar to but larger than that arising from deuteronation of coordinated alkoxide, vide infra. Admittedly, this represents an entirely empirical approach to the interpretation of pmr shifts on coordination which must be regarded as tentative and subject to reevaluation as evidence accumulates. Fortunately, the assignment of thioether as an active donor function in this complex rests as well on the broader evidence adduced previously.

Glycinatobis(ethylenediamine)cobalt(III) Perchlorate--$[Co(en)_2(OOCCH_2NH_2)](ClO_4)_2$

This compound was characterized by elemental analysis, visible and infrared spectroscopy, and ion exchange chromatography. Elemental analyses for carbon, hydrogen, nitrogen and cobalt were in good agreement with the calculated values (Experimental section). Ion exchange behavior identified the ion as a +2 species with both neutral and 0.10 M acid eluent (Table I).

Visible spectral parameters for the complex in water and 0.10 M acid are as follows: $[\lambda(\epsilon)$: 487(98), 346(106)]. The infrared spectrum exhibited intense peaks at 1,640 cm^{-1} and 1,340 cm^{-1} characteristic of coordinated carboxylate.[16,33] The spectral parameters are in good agreement with the previously prepared and reported chloride salt of the complex, $[Co(en)_2(OOCCH_2NH_2)]Cl_2$.[16]

2-Mercaptopropionatopentaaquochromium(III) Ion (Mercaptide-Bound)--$[Cr(H_2O)_5(SCH(CH_3)COOH)]^+$

The reaction of aqueous chromium(II) with $[Co(en)_2(OOCCH(CH_3)S)]^+$ is extremely rapid and results in $>90\%$ incorporation of the mercaptopropionate in the chromium(III) product coordination sphere, *vide infra*. On the basis of these observations and the high steric improbability of a doubly bridged mechanism utilizing both carboxylate oxygen and mercaptide sulfur evident in models lead to the formulation of the first product of the oxidation-reduction as $[Cr(H_2O)_5(SCH(CH_3)COOH)]^{2+}$. When the reaction of the cobalt(III) complex and chromium(II) ion is performed with a slight excess of oxidant a fleeting intermediate is observed which undergoes a rapid subsequent reaction ($k_{obs} = 3.29 \times 10^{-2}$ $\underline{M}^{-1}$ sec^{-1} at $[H^+] = 0.90$ $\underline{M}$, see kinetic description below) to produce a species spectrally identical to the chelated 2-mercaptopropionatotetraaquochromium(III) ion, a sufficiently long-lived species to be partially characterized in solution and the only isolable product of the reaction of the cobalt(III) complex in the presence of the excess chromium(II) ion.

The sulfur-bound monodentate intermediate is not sufficiently long-lived to determine its spectral parameters, but the relatively small change in absorbance observed on conversion to the chelated product suggests an anomalously high molar absorptivity for the intermediate. Since the intermediate, as formulated, is comparable to the $[Cr(H_2O)_5SH]^{2+}$ species (see Table III), the spectral observations are then reasonable and lend credence to the nature of the short-lived species as proposed.

2-Mercaptopropionatotetraaquochromium(III) Ion--$[Cr(H_2O)_4(OOCCH(CH_3)S)]^+$

The isolable product obtained from the previously descussed species or from reaction of the cobalt(III) complex with excess chromium(II) is so formulated on the basis of ion-exchange behavior and spectral parameters observed from the products of the reaction of $[Co(en)_2(OOCCH(CH_3)S)]^+$ and Cr(II), a representative example of which follows.

A 210 ml reaction mixture initially 5.0×10^{-3} $\underline{M}$ in Co(III), 5.1×10^{-3} $\underline{M}$ in Cr(II) and 0.020 $\underline{M}$ in H^+ was exposed to the air after a five-minute reaction period and charged onto a 30 cm

(1.2 cm diameter) column of Biorad-purified Dowex 50 w-x2, 200, 400 mesh, cation exchange resin in the lithium form. After a charging and washing time of about thirty minutes a +1 chromium species was eluted with 0.25 M $LiClO_4$. The band began to elute after passing about 50 ml of eluent and was collected in about 35 ml. Volume was adjusted to 100 ml with eluent serving as diluent. Aliquots of this solution were then used for further study with appropriate additions of standard $HClO_4$ and solid $LiClO_4$ to maintain the desired pH and ionic strength. Separate runs provided 90-95% recovery of the 2-mercaptopropionate-containing chromium(III) ion, on a 1:1 mole basis relative to the amount of cobalt(III) complex used initially, based on the previously described method for chromium determination, vide supra.

That this product is the chelated 2-mercaptopropionate complex is confirmed by the +1 charge and its spectral parameters [$\lambda(\epsilon)$: 545(71.2 ± 1.0), 440(52.2 ± 1.0), 265(5040 ± 150)] (the uncertainties in the molar absorptivities are due to subsequent reaction of the species, vide infra). These values compare favorably with those of mercaptoacetatotetraaquochromium(III) ion and thiolopentaaquochromium(III) ion (Table III). In both of the latter species the high energy d-d transition (440 nm) and the near-ultraviolet absorbance (265 nm, provisionally assigned to sulfur-to-metal charge transfer, vide supra, strongly suggest mercaptide coordination. The fact that the low energy d-d transition (545 nm) occurs for both acid complexes and is blue-shifted from the values for the thiolo and aquo chromium species indicates carboxylate coordination (Table III). Similar observations have been reported for several carboxylate-bound chromium(III) species.[35] The high molar absorptivities observed suggest chelation, which would lower the overall symmetry. Examination of the molar absorptivities of several cis-aquo carboxylate complexes of both cobalt(III) and chromium(III) further substantiate this explanation (Table II and III). Occurence of the sulfur-to-metal charge transfer absorbance some 20 nm higher in energy for chromium(III) complexes than for cobalt(III) complexes lends credence to the assignation of the transition to the charge transfer in view of the decreased tendency of chromium(III) to be reduced relative to that of cobalt(III), (E_o^{red} ($M^{3+/2+}$): +1.84 v (Co^{3+}/Co^{2+}), -0.41 v (Cr^{3+}/Cr^{2+})).[40]

2-Mercaptopropionatopentaaquochromium(III) Ion (Carboxylate-Bound)--$[Cr(H_2O)_5(OOCCH(CH_3)SH)]^{2+}$

Isolation in solution of this species from the direct reaction of the cobalt(III) complex and chromium(II) is not possible due to presence of the cobalt(II) ion produced. Elution characteristics of the product +2 ions are nearly the same, resulting in an ineffectual separation. However, isolation of the previously described chromium(III) chelate complex followed by subsequent reaction in various acid solutions affords a route to an equilibrium mixture of the chelate and pendant (carboxylate-bound) chromium(III) ions. This mixture can then be separated by ion exchange. Use of the ionic strength in the range 0.25 M to 0.50 M in $HClO_4$--$LiClO_4$ for the equilibrium reaction results in the chelate fraction not being retained on the column while the +2 monodentate form remains. Elution with 1.0 M $LiClO_4$ allows isolation of the monodentate form.

Because of subsequent reaction of the monodentate carboxylate ion to hexaaquochromium(III) it is not possible to recover totally the initial amount of chromium as either chelate or monodentate.

The monodentate product was characterized by its +2 charge and the similarity of its visible spectrum [$\lambda(\epsilon)$: 568(25.0 $\pm$ 1.0), 411(24.5 $\pm$ 1.0)] to previously prepared carboxylatochromium(III) ions.[35] Again a high energy peak at about 210 nm was present, but again of varying intensity ($\epsilon = 19{,}000 \pm 2{,}000$).

Upon isolation, solutions of the monodentate carboxylato product can be observed to undergo subsequent reaction spectrophotometrically. Ion exchange separation of an equilibrium mixture after several days results in three separable fractions. The first fraction elutes as a +1 ion and is spectrally identical to the original $[Cr(H_2O)_4(OOCCH(CH_3)S)]^+$ ion whereas the second fraction is the monodentate species, the +2 ion $[Cr(H_2O)_5(OOCCH(CH_3)\text{-}SH)]^{2+}$. The presence of the chelate form shows that dechelation of the chromium-sulfur bond is reversible. The third fraction was identified as $[Cr(H_2O)_6]^{3+}$.

Lactatopentaaquochromium(III) Ion (Alkoxide-Bound)--$[Cr(H_2O)_5(OCH\text{-}(CH_3)COOH)]^{2+}$

That this species is the first product formed in the reaction between aqueous chromium(II) ion and $[Co(en)_2(OOCCH(CH_3)OH)]^{2+}$ at pH = 3.4 (where the alcohol function is substantially deprotonated) or of the path inversely proportional to hydrogen ion concentration at low pH, vide infra, follows logically in comparison with the sulfur analogue. The ion has not been independently identified, however.

Lactatopentaaquochromium(III) Ion (Carboxylate-Bound)--$[Cr(H_2O)_5(OOCCH(CH_3)OH)]^{2+}$

From the reaction of $[Co(en)_2(OOCCH(CH_3)OH)]^{2+}$ (1.0×10^{-2} M), with chromium(II) (1.1×10^{-2} M) in 0.100 M $HClO_4$, a dipositive chromium(III) product, characterized as the monodentate lactato complex, can be isolated using ion exchange techniques. The visible spectrum in 0.10 M $HClO_4$ had the following parameters: $[\lambda(\epsilon)$: 568(26.8 ± 1.0), 412(33.2 ± 1.0)$]$. The molar absorptivities are slightly higher than previously reported values of 25.7 and 31.2 for the respective peaks,[41] but it should be noted that the complex was not isolated in the previous work and values are based on 35% complexation in a solution of lactate and chromium(III) ion. It should be noted further that the peak ratios reported previously ($\epsilon_{\lambda_1}/\epsilon_{\lambda_2} = 0.82$) do agree reasonably well with values observed in this work, ($\epsilon_{\lambda_1}/\epsilon_{\lambda_2} = 0.81$).

When the reaction of $[Co(en)_2(OOCCH(CH_3)OH)]^{2+}$ was performed at an initial acidity of 4.0×10^{-4} M $HClO_4$, two chromium(III)-containing complexes of the lactate were eluted from the cation exchange column in the approximate molar ratio of 2:1. The first and major fraction was eluted with neutral eluent as a pink +1 ion described below. The second fraction eluted with the same neutral eluent as a +2 ion that changed over short but observable periods from a blue color on the column to a pink color in solution with a spectrum identical to that of the first fraction (pH = 2.9). The blue species may be the alkoxide-bound monodentated complex but its fleeting existence makes this characterization tentative. Acidification of both fraction to pH = 1 gave the spectrum of the monodentate species within the time span necessary for the experiment (5-10 min).

From the fact that the +2 and +1 ions are readily interconvertible at a measurable rate, vide infra, it can be surmised that the +1 ion is not the $[Cr(H_2O)_4(OH)(OOCCH(CH_3)OH)]^+$ complex for two reasons: (1) The pK_a of the carboxylate-bound +2 lactato complex would be expected to be near that of the acetato analogue, $[Cr(H_2O)_5(OOCCH_3)]^{2+}$, that is, $pK_a = 4.5$.[25] (2) If the hydroxy complex were important, its formation would be expected to be diffusion controlled.

Lactatotetraaquochromium(III) Ion--$[Cr(H_2O)_4(OOCCH(CH_3)O)]^+$

This chelated species was concluded to be the major product observed (~65%) from the reaction of $[Co(en)_2(OOCCH(CH_3)O)]^+$ and chromium(II) at pH = 3.4. Cation exchange separation characterized the species as a +1 ion which had spectral parameters of [$\lambda(\epsilon)$: 548(31.2), 437(38.1)] at pH = 2.8. Subjecting the monodentate carboxylato species to pH = 2.8 resulted in a change producing similar spectral parameters based on total chromium(III), [$\lambda(\epsilon)$: 548(31 ± 2), 437(37 ± 2)], within the five minutes necessary for manipulation.

Examination of the spectral parameters of the proposed chelate complex and comparison to the analogous mercaptopropionate complex, which appears more solidly formulated, supports the chelate form for the +1 complex. The energies for the d-d transitions are essentially identical for both the alkoxide and mercaptide complexes of chromium(III) (Table III) as is found to be the case for the cobalt(III) complexes (Table II). The red-shifting of the high energy band and blue-shifting of the low energy band relative to chromium(III) occur in the regions expected for coordination through alkoxide and carboxylate but not expected for coordination of either function alone. Finally, the observed molar absorptivity would be anomalously high for chromium(III) complexes bound through carboxylate alone in comparison to similar complexes.[35]

Methylthioacetatopentaaquochromium(III) Ion (Thioether-Bound)--$[Cr(H_2O)_5(S(CH_3)CH_2COOH)]^{2+}$

By comparison to the mercaptide complex, this species is expected to be the first product formed in the reaction between aqueous chromium(II) ion and $[Co(en)_2(OOCCH_2SCH_3)]^{2+}$. Since the ion has not been independently identified and its formulation is based on kinetic results, discussion of it will be deferred to the appropriate section.

Methylthioacetatotetraaquochromium(III) Ion--$[Cr(H_2O)_4(OOCCH_2SCH_3)]^{2+}$

Formulation of this ion as the product of a subsequent reaction of the thioether-bound monodentate species described above is based on kinetic results and will therefore be discussed in a later section.

Methylthioacetatopentaaquochromium(III) Ion (Carboxylate-Bound)--$[Cr(H_2O)_5(OOCCH_2SCH_3)]^{2+}$

This species can be isolated in solution in >90% yield using cation exchange techniques from the reaction of $[Co(en)_2(OOCCH_2SCH_3)]^{2+}$ with chromium(II) ion with the latter in deficiency, equivalency or excess. The species is formulated as a +2 ion on the basis of ion exchange elution behavior (Table II). The visible spectrum in 0.50 M $LiClO_4$, pH = 3.4, exhibited the following parameters: [$\lambda(\epsilon)$: 567(26.7), 412(25.9)]. The visible spectrum was found to be quite similar to that of the $[Cr(H_2O)_5(OOCCH_2SH)]^{2+}$ and other carboxylato-chromium(III) species (Table III), thus confirming formulation of the ion as described. The +2 ion is the only observable product of the reaction of $[Co(en)_2(OOCCH_2SCH_3)]^{2+}$ and Cr(II) at acid concentrations in the range 0.10 M to 0,10 M.

Glycinatopentaaquochromium(III) Ion (Carboxylate-Bound)--$[Cr(H_2O)_5(OOCCH_2NH_3)]^{3+}$

This species can be isolated in solution in > 90% yield using cation exchange techniques from the reaction of $[Co(en)_2(OOCCH_2NH_2)]^{2+}$ with chromium(II) with the latter in deficiency, equivalency or excess. The blue product is formulated as a +3 ion on the basis of ion exchange elution behavior (Table I). The visible spectrum in 1.0 M $LiClO_4$, pH = 3.5 exhibited the following parameters: [$\lambda(\epsilon)$: 573(22.0 ± 1.0), 412(23.0 ± 1.6)]. Although the peak positions are quite similar to $[Cr(H_2O)_6]^{3+}$, the molar absorptivities eliminate the possibility of this complex as a product (Table III). Spectral comparison to other carboxylato-chromium(III) species confirms formulation of the ion as described. The +3 ion is the only observable product of the reaction of $[Co(en)_2(OOCCH_2NH_2)]^{2+}$ and Cr(II) at acid concentrations in the range 0.1 M to 1.0×10^{-4} M.

Glycinatotetraaquochromium(III) Ion--$[Cr(H_2O)_4(OOCCH_2NH_2)]^{2+}$

Upon adjustment of the pH to 4.5 of a solution of the glycinato(carboxylate-bound)-chromium(III) species described above, the solution color changed rapidly from blue to green, but the maxima of the visible absorptions remained essentially constant. Letting the solution equilibrate for several days resulted in the solution acquiring a red-violet hue. The higher energy absorption remained very nearly at its previous position, but the low energy absorption shifted to 560 ± 5 nm. On passing the equilibrated solution through a cation exchange column in the lithium form, it was noticed that a faintly colored fraction was not retained on the column, probably due to the high ionic strength (1.0 $\underline{M}$) of the charging solution. Collection of this fraction and spectral analysis yielded the following: [$\lambda(\epsilon)$: 555(38.0 ± 5), 420(41.0 ± 6)]. From the high molar absorptivities compared to carboxylate-bound chromium(III) species but relatively normal for chelate species (Table III), the spectral shift of the low energy band to higher energy and the fact that the ion was not retained on the cation exchange column, it is tentatively concluded that the species is the chelated $[Cr(H_2O)_4(OOCCH_2NH_2)]^{2+}$ ion.

Reactions of Chromium(II) with the Cobalt(III) Complexes

2-Mercaptopropionatobis(ethylenediamine)cobalt(III) Ion--$[Co(en)_2(OOCCH(CH_2)S)]^+$

The stoichiometry of this reaction was determined by ion exchange separation of the reaction products followed by chromium analysis of the appropriate fraction. Several reactions were carried out having reductant and oxidant alternatively in excess. A solution of chromium(II) was injected into solutions of the complex with the usual exclusion of air. Within fifteen minutes the reaction mixture was exposed to the air and charged onto a suitably prepared column. In each case the amount of chromium(III) product elutable as a +1 ion closely approximated that of the deficient reactant (Table V). This is indicative that the oxidant and reductant react in equimolar amounts. This first isolable product was characterized as the chelated chromium(III) product, $[Cr(H_2O)_4(OOCCH(CH_3)S)]^+$, _vide supra_. The fact that the ligand is ~100% incorporated in the product at varying reactant ratios is taken to establish the reaction as inner-sphere in nature.[42] As previously discussed, the chelated +1 ion was concluded to be a secondary product of the initial oxidation-reduction reaction, the result of the ring closure of the primary monodentate product, $[Cr(H_2O)_5(S(CH_3)CHCOOH)]^{2+}$. The only other chromium-containing fraction was obtained from reactions with reductant in excess and was characterized spectrally as the air-oxidized dimer of chromium(III).[43] Spectra of the product solutions corresponded within 4% to those calculated based on a 1:1 stoichiometry and summing the contributions of each species remaining.

The rate of the Cr(II)-$[Co(en)_2(OOCCH(CH_3)S)]^+$ reaction was found to be measurable on the stopped-flow instrument. Since the second-order rate constant was $>10^5$ ($\underline{M}^{-1}$ sec^{-1}) it was necessary to follow the disappearance of the sulfur-to-metal charge transfer peak in the near-ultraviolet region. Here advantage could be taken of the high (~12,000) molar absorptivity which allowed solutions of extremely low concentration to be used.

TABLE V

Stoichiometries of the Reactions of Cobalt(III) Complexes with Chromium(II)

Co(III)L mmole	Cr(II) mmole	$[H^+]$ $\underline{M}$	$Cr(III)L^+$ mmole	$Cr(III)L^{2+}$ mmole	$Cr(III)L^{3+}$ mmole
		L = 2-Mercaptopropionate			
0.241	0.450	0.100	.214	--	--
1.00	1.00	0.0100	.933	--	--
0.245	0.150	0.100	.141	--	--
		L = Lactate			
0.251	0.500	0.100	--	.240	--
0.244	0.250	0.100	--	.232	--
0.249	0.150	0.100	--	.141	--
0.050[a]	0.050	4.0×10^{-4}	.0047	.0023	--
		L = Methylthioacetate			
0.102	0.175	0.100	--	.089	--
0.100	0.094	0.100	--	.086	--
0.092	0.065	0.100	--	.065	--
		L = Glycinate			
0.202	0.400	0.100	--	--	.190
0.205	0.208	0.100	--	--	.190
0.143	0.064	0.100	--	--	.060

[a] Reaction incomplete after 15 hours.

In a typical experiment, solutions of cobalt(III) complex at 3.75×10^{-6} M and chromium(II) at 5.4×10^{-4} M each at $H^{+} =$ 1.0×10^{-2} M and with ionic strength maintained at 0.10 M with $LiClO_4$ were deaerated while thermostatted, then transferred to the drive syringes of the stopped-flow instrument as previously described. Use of these concentrations allows the data obtained to be treated as a pseudo-first-order reaction. Thus, a plot of log $(A_t - A_\infty)$ vs time permitted calculation of an observed rate constant which then could be converted to the second-order rate constant. For the concentrations specified, the reaction was complete in 20 msec. To ascertain the dependence, or lack thereof, on acid concentration and order of the reaction with respect to chromium(II) ion, each was varied independently over a ten-fold range while other variables remained constant. It was found that the reaction is independent of the acid concentration in the range $[H^{+}] = 0.10$ M to $[H^{+}] = 0.010$ M and first-order in chromium(II) ion in the range $[Cr(II)] = 2.15 \times 10^{-3}$ M to $[Cr(II)] = 2.15 \times 10^{-4}$ M (Table VI). By virtue of the linearity of the log $(A_t - A_\infty)$ vs t plots over at least three half-lives (>90% reaction) it was concluded that the reaction is also first order in oxidant. The second-order rate constant for the reaction of $[Co(en)_2(OOCCH(CH_3)S)]^{+}$ with chromium(II) was found to be $(1.55 \pm 0.25) \times 10^{5}\ M^{-1}\ sec^{-1}$.

Lactatobis(ethylenediamine)cobalt(III) Ion--$[Co(en)_2(OOCCH(CH_3)\text{-}O(H))]^{+(2+)}$

The stoichiometry of this reaction was found to be approximately equimolar in each reactant at $[H^{+}] = 0.010$ M (Table V) by

TABLE VI

Acid and Chromium(II) Dependencies of the Reactions of Some Cobalt(III) Complexes with Chromium(II)

$[Co(III)L]^n$ M x 10^5	$[Cr(II)]$ M x 10^3	$[H^+]$ M	k_{obs} M^{-1} sec^{-1}
	L = 2-Mercaptopropionate[a]		
0.40	1.05	0.100	1.60×10^5
0.40	1.05	0.010	1.55×10^5
0.40	2.15	0.010	1.61×10^5
0.40	0.54	0.010	1.32×10^5
0.40	0.21	0.010	1.46×10^5
	L = Methylthioacetate[b]		
13.6	47.0	0.100	267
13.6	47.0	0.050	271
13.6	47.0	0.010	281
13.6	98.0	0.100	264
13.6	9.4	0.100	286
	L = Glycinate[b]		
48.0	8.40	0.100	2.22
48.0	8.40	0.010	2.26
48.0	98.0	0.100	2.05

[a] μ = 0.100 M ($LiClO_4$--$HClO_4$). [b] μ = 1.00 M ($LiClO_4$--$HClO_4$).

methods analogous to those used in the preceding section. The reaction was found to proceed by two different pathways, vide infra, but usually only one chromium-containing product was **isolable** from a given reaction. It has been found that the initial chromium-containing product of the reaction exists in two rapidly interconvertible forms, vide infra.

By methods similar to those described for the mercaptide analogue it was determined that the oxidation-reduction reaction was first order in each reactant by pseudo-first-order techniques (Table VII). It was possible to follow the disappearance of the protonated form of the cobalt(III) complex by spectrophotometric monitoring of its absorption maximum at 499 nm on the stopped-flow instrument. Again linearity over >90% of the reaction was observed for the kinetic plots. The second-order rate constant for this complex was found, however, to vary inversely with acidity over the range 1.0 M $\leq [H^+] \geq 6.7 \times 10^{-3}$ M (Table VII). A plot of k_{obs} vs $[H^+]^{-1}$ was linear (Figure 1) and yielded the expression for the rate constant as

$$k = \frac{7.35 + 0.023\,[H^+]^{-1}}{1 + K_{eq}[H^+]^{-1}} \quad (\underline{M} \text{ and sec})$$

This observation can be understood from a rigorous solution of the differential rate equation for this reaction[10]

$$\frac{-d[Co(III)]total}{dt} = k_{obs}[Co(III)]total \qquad (13)$$

where K_a is the acid dissociation constant of $[Co(en)_2(OOCCH(CH_3)\text{-}OH)]^{2+}$ and k_1 and k_2 are defined by

TABLE VII

Acid and Chromium(II) Dependence of the Reduction of $[Co(en)_2(OOCCH(CH_3)OH)]^{2+}$ by Chromium(II)

[Co(III)] x 10^4 M	[Cr(II)] x 10^3 M	$[H^+]$ M	k_{obs} M^{-1} sec^{-1}
2.00	68.0	.0100	9.15
2.00	5.50	.0100	9.62
2.00	5.50	1.000	7.21
2.00	5.50	.1020	7.50
2.00	5.50	.0507	8.10
2.00	5.50	.0167	8.70
2.00	5.00	.0067	10.77
.10	1.00	8.00×10^{-5}	47*

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*Approximate value; variations between separate reactions > 20%.

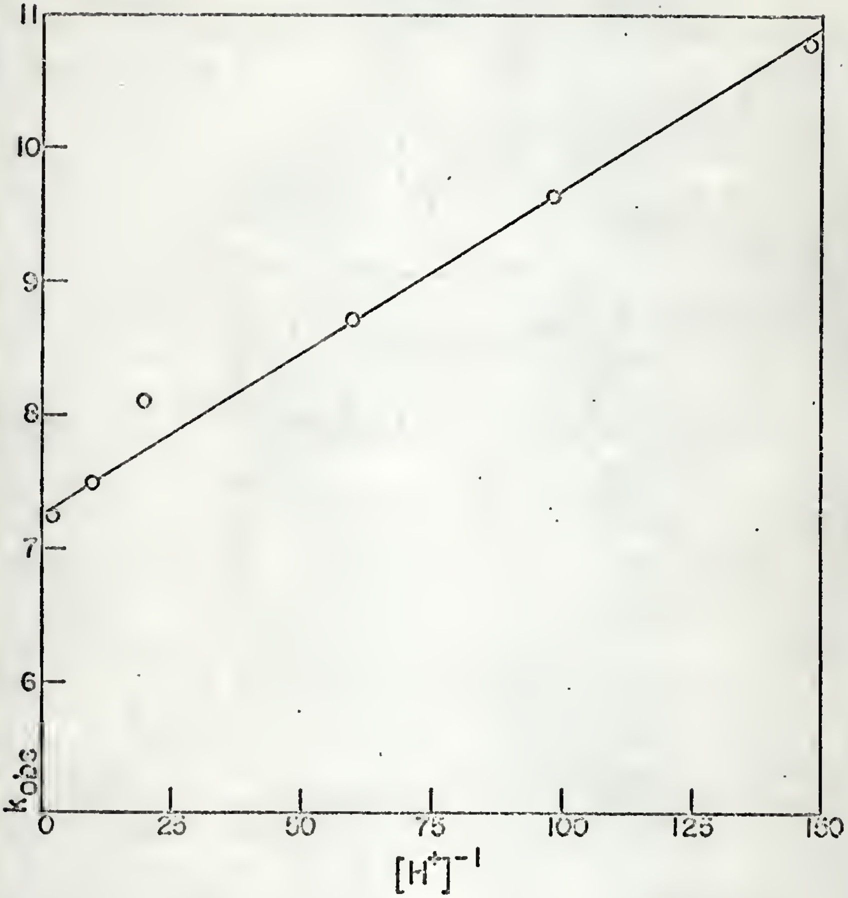


Figure 1. Acid dependence of the reduction of $[Co(en)_2(OOCCH(CH_3)OH)]^{2+}$ by chromium(II).

$$[Co(en)_2(OOCCH(CH_3)OH)]^{2+} + Cr^{2+} \xrightarrow{k_1} \text{products}$$

$$[Co(en)_2(OOCCH(CH_3)O)]^{+} + Cr^{2+} \xrightarrow{k_2} \text{products}$$

From graphical analysis k_2K_a is found to be 2.3×10^{-2} and K_a determined to be 4.4×10^{-4}, vide supra, leading to the calculation of $k_2 = 52$. Several experiments were performed at $[H^+] = 8.0 \times 10^{-5}$ M where the ratio of deprotonated to protonated forms is ~5 with the observed rate being ~47. The large uncertainty in rates (>20%) encountered at this acidity level, probably due to consumption of protons by the free ethylenediamines released in the reaction, renders the values approximate. Their usefulness is limited to the observation that as the concentration of the deprotonated form is increased the observed rate constant approaches the predicted value.

From the observed rate law it is obvious that at 0.100 M acid the immediate product should arise almost exclusively via the k_1 path. As the acid concentration decreases, however, the product of the second path should appear and become dominant at extremely low acid concentration. At 0.100 M acid $[Cr(H_2O)_5(OOCCH(CH_3)OH)]^{2+}$ is the only isolable product. By using a large volume and extremely low concentrations of reactants over a long period of time, it is possible to observe both the +1 and +2 products in a molar ratio of 2:1 at a pH = 1.0×10^{-4} M.

The fact that both products are isolable from the reaction is not sufficient to confirm their genesis by two separate mechanistic pathways since both products are subject to subsequent reactions over the time period needed for the reaction and isolation period. In fact, their rapid interconversion as a function of acidity, vide infra, over a time period much shorter than that required for isolation suggests a thermodynamic rather than a kinetic distribution of products. Further consideration of the mechanism is postponed until after the rates of substitution are presented.

2-Methylthioacetatobis(ethylenediamine)cobalt(III) Ion--$[Co(en)_2(OOCCH_2SCH_3)]^{2+}$

Using the ion exchange techniques previously detailed, the stoichiometry of the reaction between chromium(II) and this ion was found to be equimolar (Table V). The only isolable reaction product was characterized as a +2 ion (Table I) and assigned the structure $[Cr(H_2O)_5(OOCCH_2SCH_3)]^{2+}$ based on its spectrum (Table III). As will be discussed in the appropriate section, this species was concluded to be a tertiary product of the initial oxidation-reduction reaction, the result of ring closure and subsequent dechelation of the primary monodentate product, $[Cr(H_2O)_5(CH_3SCH_2COOH)]^{2+}$.

The rate of the electron transfer reaction between this cobalt(III) complex and chromium(II) was found to be conveniently measurable on the stopped-flow instrument. The decrease in absorbance at 499 nm was followed spectrophotometrically under pseudo-first-order conditions allowing data to be conveniently evaluated, vide supra. A typical reaction was under conditions similar to or the same as the following: $[Co(III)] = 1.3 \times 10^{-4}$ M, $[Cr(II)] = 4.70 \times 10^{-2}$ M, $[H^+] = 0.100$ M and ionic strength maintained at 1.00 M ($HClO_4$--$LiClO_4$).

As for the previously described cobalt(III) complexes, acid concentration and chromium(II) concentration were varied independently over at least a ten-fold range to evaluate the dependence of the reaction on these two variables. Linearity of log $(A_t - A_\infty)$ vs t plots over at least 90% reaction for the ranges $[H^+] = 0.100$ M to 0.0100 M and $[Cr(II)] = 9.8 \times 10^{-2}$ M to 9.4×10^{-3} M with no significant deviation in observed rate constant leads to the conclusion that the electron transfer reaction is first order in both oxidant and reductant and independent of the acidity within the ranges specified. The calculated second-order rate constant was found to be (267 ± 18) M^{-1} sec^{-1} (Table VIII).

Glycinatobis(ethylenediamine)cobalt(III) Ion--$[Co(en)_2(OOCCH_2NH_2)]^{2+}$

The stoichiometry of this reaction was determined by ion exchange separation of the reaction products as described previously. The elution characteristics of the product are those of a +3 ion (Table I). Due to the longer reaction time relative to the three previously discussed complexes, the possiblity of loss of the primary product must be considered. Still, recoverable amounts of the only isolable product, characterized as $[Cr(H_2O)_5(OOCCH_2NH_3)]^{3+}$, vide supra, approach closely those expected for equimolar stoichiometry over the range of reactant concentrations considered (Table V).

The rate of the $[Co(en)_2(OOCCH_2NH_2)]^{2+}$-Cr(II) reaction was found to be conveniently measurable using the all-glass apparatus with the Cary 14 instrument as described in the Experimental section. A typical reaction was with solutions 4.8×10^{-4} M in the

TABLE VIII

Rate Constants for Reactions of Co(III) Complexes with Chromium(II)

Species	[Co(III)] M x 10^5	[Cr(III)] M x 10^3	$[H^+]$ M	T C	k_{obs} M^{-1} sec^{-1}
$[Co(en)_2(OOCCH(CH_3)S)]^{+}$ [a]	.40	1.05	0.010	25.0	(1.53 ± .06) x 10^5
	.40	1.05	0.010	30.1	(1.56 ± .13) x 10^5
	.40	1.05	0.010	39.1	(1.72 ± .07) x 10^5
	.40	1.05	0.010	44.6	(1.82 ± .25) x 10^5
$[Co(en)_2(OOCCH(CH_3)OH)]^{2+}$ [b]	43.2	8.40	1.00	14.0	5.96 ± .10
	43.2	8.40	1.00	25.2	8.34 ± .65
	43.2	8.40	1.00	34.0	10.72 ± .18
$[Co(en)_2(OOCCH_2SCH_3)]^{2+}$ [b]	13.6	47.0	0.100	19.9	211 ± 11
	13.6	47.0	0.100	25.0	267 ± 18
	13.6	47.0	0.100	30.2	356 ± 10
	13.6	47.0	0.100	36.7	489 ± 10
$[Co(en)_2(OOCCH_2NH_2)]^{2+}$ [b]	50.0	8.50	0.100	13.5	1.15 ± .06
	50.0	8.50	0.100	25.0	2.22 ± .12
	50.0	8.50	0.100	34.1	3.52 ± .13

[a] μ = 0.100 M ($LiClO_4$--$HClO_4$). [b] μ = 1.00 M ($LiClO_4$--$HClO_4$).

cobalt complex and 8.4 x 10^{-3} $\underline{M}$ in Cr(II) at $[H^+] = 1.00 \times 10^{-2}$ $\underline{M}$ (ionic strength maintained at 1.00 $\underline{M}$ with $LiClO_4$). These were transferred anaerobically to the glass mixing apparatus which was thermostatted prior to reaction. Again pseudo-first-order conditions were maintained and the data treated appropriately.

In order to determine the acid dependence the $[H^+]$ was varied from 0.100 $\underline{M}$ to 0.0100 $\underline{M}$ with [Cr(II)], [Complex] and ionic strength constant. The order of the reaction with respect to [Cr(II)] was confirmed by use of the stopped-flow instrument with acid, complex and ionic strength constant and $[Cr(II)] = 9.00 \times 10^{-2}$ $\underline{M}$. Results are summarized in Table VI. In the specified ranges the reaction was found to be first order in oxidant and reductant and independent of the acidity. The second-order rate constant was determined to be (2.22 ± 0.12) $\underline{M}^{-1}$ sec^{-1} (Table VIII).

Activation Parameters for the Reaction Between the Cobalt(III) Complexes and Chromium(II)

Activation parameters for the reaction of the cobalt(III) complexes and chromium(II) were obtained by determination of the second-order rate constants for the individual reactions at temperatures varying from 13°C to 45°C, depending on the system. A plot of log $(k_{2nd\ order}/T)$ $\underline{vs}$ 1/T was made as previously described. At least three determinations at each of three different temperatures were made. Temperature was maintained at ± 0.10°C by methods previously described. For the reactions at other than 25.0°C, solutions were thermostatted for at least one hour prior to transference to the reaction vessels and further thermostatted there for at least one-half hour prior to reaction. Rate constants so obtained for the four cobalt(III) complexes are summarized in Table VIII.

Average values at each temperature were used to determine the respective activation parameters via a least squares analysis. Plots so obtained are shown in Figures 2, 3 and 4. Error limits for the activation parameters were determined from the most deviant lines still encompassed by all rate error limits. Results are summarized in Table IX.

Attempts to determine activation parameters for reaction involving the deprotonated form of the Co(III) lactate complex were abandoned due to a >20% fluctuation in reproduciblity at $[H^+] = 8.0 \times 10^{-5}$ $\underline{M}$ where the deprotonated form is dominant. This resulted in overlapping values of k_{obs} at the various temperatures. At intermediate pH levels distinct curvature in the Eyring plots was observed. This curvature could arise from different activation enthalpies for the two contributing paths as well as from an expected variation in K_a with temperatures. Thus, values at the lower pH values would not realistically measure the activation energy for the deprotonated form without a determination of K_a and the acid dependence at each temperature which was not done.

Substitution Reactions of the Chromium(III) Products

2-Mercaptopropionate as Ligand

Using a slight excess of $[Co(en)_2(OOCCH(CH_3)S)]^+$ relative to

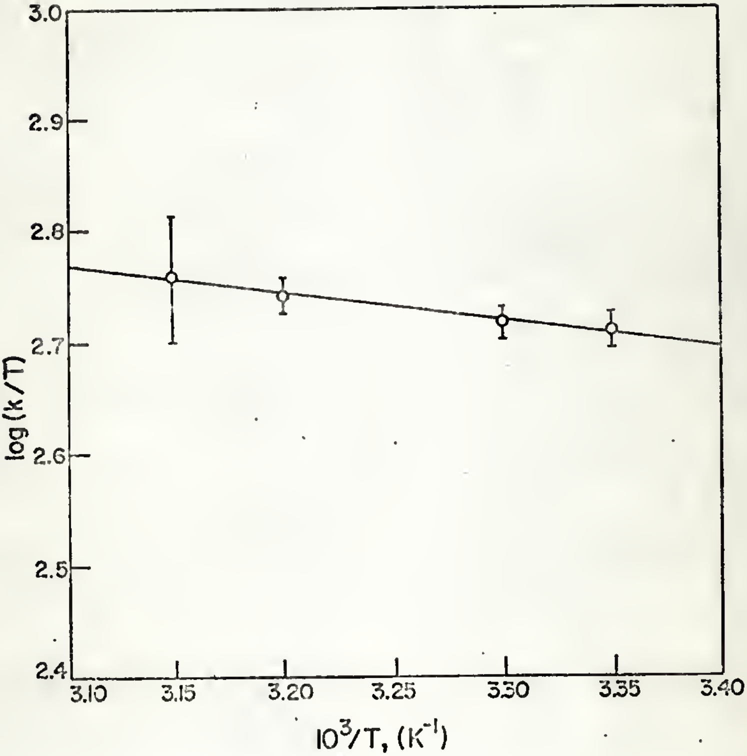


Figure 2. Eyring plot for $[Co(en)_2(OOCCH(CH_3)S)]^+$.
μ = 0.100 M ($HClO_4$--$LiClO_4$).

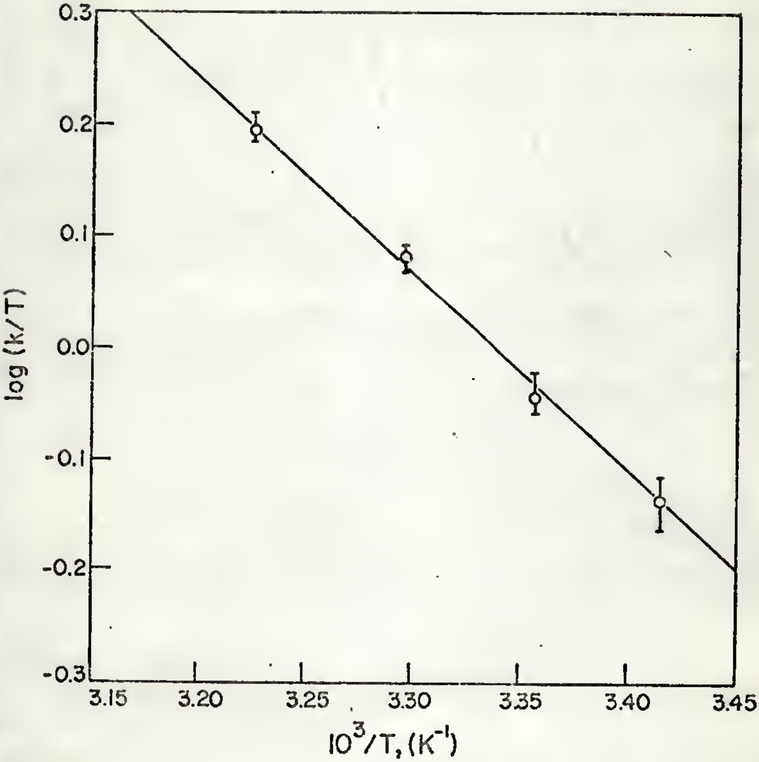


Figure 3. Eyring plot for $[Co(en)_2(OOCCH_2SCH_3)]^{2+}$. μ = 1.00 M ($HClO_4$--$LiClO_4$).

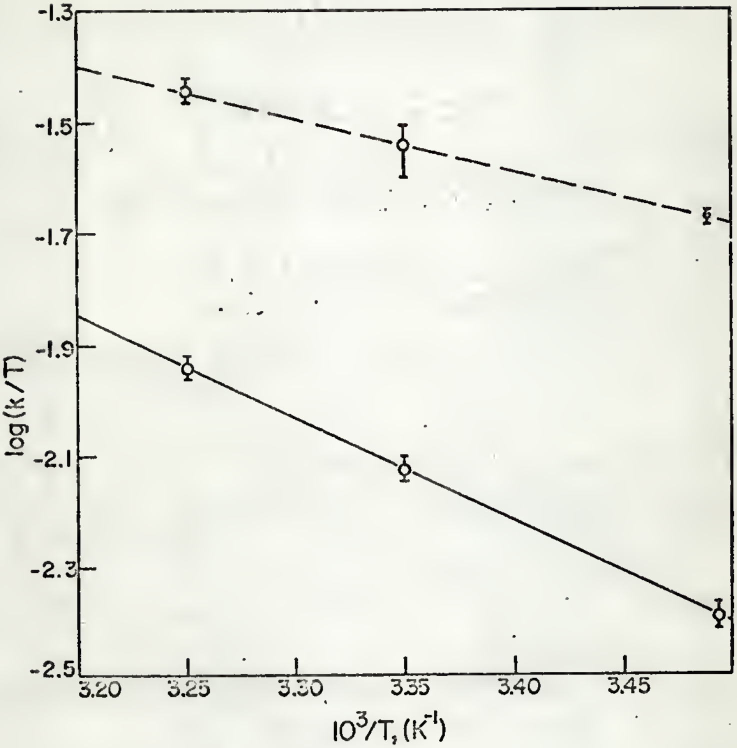


Figure 4. Eyring plots for some cobalt(III) complexes.

—— $[Co(en)_2(OOCCH_2NH_2)]^{2+}$

---- $[Co(en)_2(OOCCH(CH_3)OH)]^{2+}$

μ = 1.00 M ($HClO_4$--$LiClO_4$).

TABLE IX

Activation Parameters for the Reactions of Chromium(II) with Cobalt(III) Complexes

Complex	$\Delta H^{\ddagger}$ Kcal mole^{-1}	$\Delta S^{\ddagger}$ cal deg^{-1}	$\Delta G^{\ddagger\, a}$ Kcal mole^{-1}
$[Co(en)_2(OOCCH(CH_3)S)]^{+\ b}$	1.1 ± 1.7	-31.1 ± 5.7	1.04 ± 3.4
$[Co(en)_2(OOCCH(CH_3)OH)]^{2+\ c}$	4.7 ± 0.4	-39.1 ± 1.0	16.4 ± 0.8
$[Co(en)_2(OOCCH_2SCH_3)]^{2+\ c}$	8.5 ± 0.8	-18.9 ± 2.5	11.2 ± 3.5
$[Co(en)_2(OOCCH_2NH_2)]^{2+\ c}$	8.8 ± 0.8	-27.4 ± 2.6	17.0 ± 1.6

[a] T = 25.0°C. [b] μ = 0.10 $\underline{M}$ ($HClO_4$--$LiClO_4$). [c] μ = 1.00 $\underline{M}$ ($HClO_4$--$LiClO_4$).

chromium(II) at high acid concentration, the stopped-flow instrument can be used to measure the rate of the first reaction subsequent to the initial redox reaction. This secondary reaction was followed by monitoring the increase in absorbance at 545 nm, a maximum for the chelated 2-mercaptopropionate chromium(III) complex. This subsequent reaction has been postulated as the ring closure reaction of $[Cr(H_2O)_5(S(CH_3)CHCOOH)]^{2+}$ (mercaptide-bound), the initial product of the redox reaction, vide supra.

The first experimentally isolable product of the redox reaction under all conditions has been characterized as the chelated chromium(III) product of this ring closure, $[Cr(H_2O)_4(OOCCH(CH_3)S)]^+$, vide supra. This product underwent a subsequent reaction over a twenty-four-hour period which was then separated via ion exchange to yield mostly +1 and +2 ions with some small amount of a +3 ion also present, especially a low acid concentration (< 0.20 M). The +1 ion exhibited identical spectral parameters to the original chelated complex, $[Cr(H_2O)_4(OOCCH(CH_3)S)]^+$, while the +2 fraction was spectrally identical to the monodentate complex, $[Cr(H_2O)_5(OOCCH(CH_3)SH)]^{2+}$. The +3 ion was spectrally identified as $[Cr(H_2O)_6]^{3+}$. By spectrophotometric monitoring of the 264 nm absorption it can be shown that the +2 fraction converts back to the chelate form. This peak has been assigned to a metal-coordinated mercaptide chromophore on the basis of its presence in the chelate complex, absence in the monodentate carboxylate-bound complex and similarity in energy and molar absorptivity to other chromium(III)-mercaptide species (Table III). These observations can be understood by consideration of the following net ionic reactions and observed rate laws at constant acidity.

$$[Co(en)_2(OOCCH(CH_3)S)]^+ + Cr^{2+} + 5H^+ \rightarrow$$

$$[Cr(H_2O)_5(SCH(CH_3)COOH)]^{2+} + Co^{2+} + 2enH_2^{\ 2+} \qquad (A)$$

I

$$I \xrightarrow{k} [Cr(H_2O)_4(OOCH(CH_3)S)]^+ \qquad (B)$$

II

$$II + H^+ \underset{k_r}{\overset{k_f}{\rightleftharpoons}} [Cr(H_2O)_5(OOCCH(CH_3)SH)]^{2+},\ K_{eq} \qquad (C)$$

III

$$\frac{d[II]}{dt} = -k_f[II] + k_r[III],\ k_{obs} = k_f + k_r$$

The rate of the initial process (B) to form II varied linearly with acidity: A plot of k *vs* $[H^+]$ (Figure 5) where $[H^+]$ is varied from 0.900 M to 0.0900 M results in the expression $k = (1.0 + 2.6\,[H^+]) \times 10^{-2}$ (M and sec, $\mu = 1.00$ M ($HClO_4$--$LiClO_4$), 25°C).

A determination of the K_{eq} for reaction (C) was necessary in order to evaluate k_f and k_r, *vide supra*. K_{eq} was determined by allowing a solution of II to equilibrate at known acidities. The equilibration was followed spectrophotometrically at 545 nm, a maximum for II, over a twenty-to thirty-hour period with readings taken every two thousand seconds for the first twenty hours. Since the hydrolysis of III to $[Cr(H_2O)_6]^{3+}$ marginally overlaps the equilibration, a plot of A_{obs} *vs* time was then used to evaluate the absorbance at equilibrium. A_{eq} was closely approximated by extrapolation of the very gradually decreasing terminal portion of this

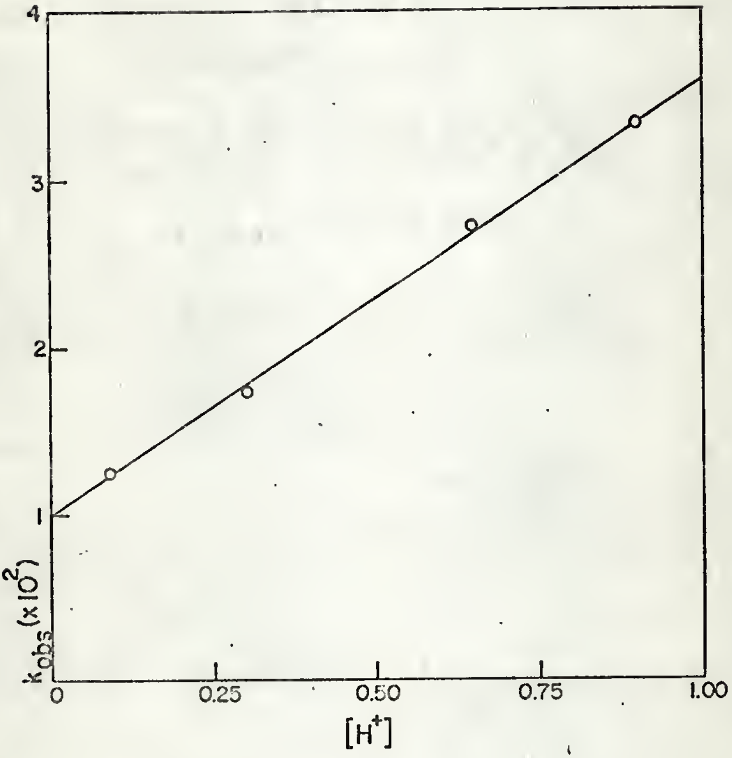


Figure 5. Acid dependence of ring closure of $[Cr(H_2O)_5(SCH(CH_3)COOH)]^{2+}$.

plot to t = 0 sec. This allowed a close approximation of K_{eq} from the known molar absorptivities of II and III and the acidity. The average value for three determinations gave $K_{eq} = 10.5$ (Table X). The slow hydrolysis of III to $[Cr(H_2O)_6]^{3+}$ ($k = 10^{-7}$ sec^{-1}) gives rise to a small inherent error in the K_{eq} evaluations.

The evaluation of k_f and k_r was accomplished starting with solutions of II for the sake of convenience. The observed conversion of III to II could have been used alternatively. The acidity range examined was dictated by side reactions at higher pH to be examined further and discussed elsewhere.

The evaluation of k_{obs} at a given acidity was accomplished by plotting log $(A_t - A_{eq})$ vs t. The plots were found to be linear over at least two half-lives. For reactions with $[H^+] < 0.30$ M, A_{eq} was calculated from the value of K_{eq}, the acidity, initial concentration of II and the respective molar absorptivities of II and III. Values of k_f and k_r were then calculated from k_{obs}, K_{eq} and $[H^+]$ by methods previously described.

Within the range $[H^+] = 0.65$ M to 0.100 M, k_f was found to vary linearly with acid concentration while k_r was independent of acid concentration (Table XI). Plots of k_f vs $[H^+]$ (Figure 6) and k_r vs $[H^+]^{-1}$ (Figure 7) gave the following rate expressions:

$$k_f = (7.31\,[H^+]) \times 10^{-5} \quad (\underline{M} \text{ and sec})$$

$$k_r = 7.10 \times 10^{-6} \quad (\underline{M} \text{ and sec})$$

Error limits for the respective plots of k_f and k_r were obtained from the error limits in K_{eq} and evaluation of k_f and k_r based on the maximum deviation values.

TABLE X

Evaluation of Equilibrium Constant for the Chromium(III)-2-Mercaptopropionate Interconversion[a]

$[H^+]$ M	$[CrL^+]$ M x 10^3	$[CrL^{2+}]_{eq}$ M x 10^3	K_{eq}
1.00	0.11	1.29	11.7
0.500	0.23	1.17	10.2
0.300	0.35	1.05	9.7
			Avg = 10.5 ± 1.2

[a] μ = 1.00 M ($HClO_4$--$LiClO_4$), 25°C, 100 ml solution.

TABLE XI

Acid Dependence for Interconversion of the Chromium(III)-2-Mercaptopropionate[a]

$[H^+]$ M	k_{obs} x 10^5 sec^{-1}	k_f x 10^5 sec^{-1}	k_r x 10^6 sec^{-1}
1.00	9.34	8.51 ± .05	8.11 ± .67
0.650	5.85	5.12 ± .05	7.45 ± .60
0.500	4.26	3.57 ± .05	6.83 ± .52
0.300	2.95	2.24 ± .05	7.12 ± .50
0.180	2.04	1.34 ± .04	7.07 ± .44
0.100	1.47	0.75 ± .04	7.16 ± .37

[a] μ = 1.00 M ($HClO_4$--$LiClO_4$), 25°C.

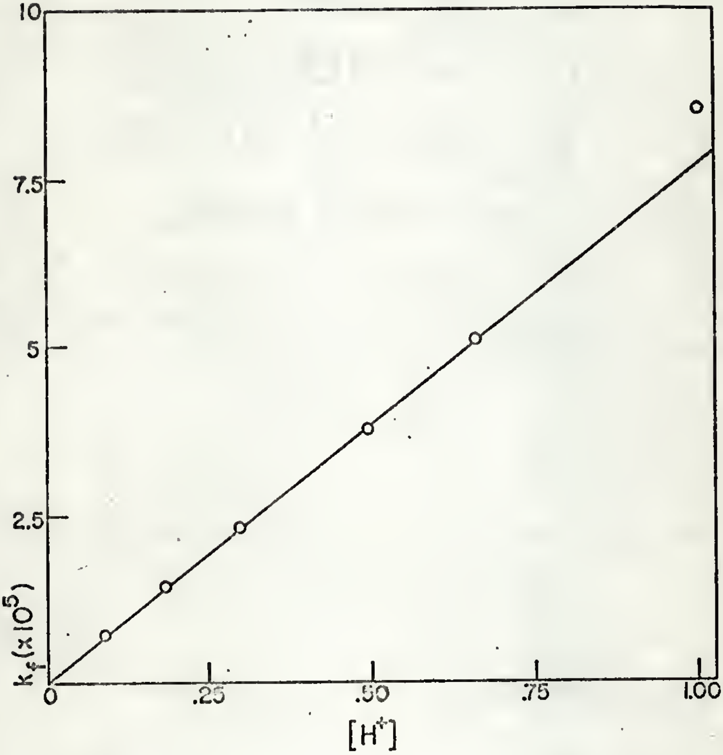


Figure 6. Acid dependence of ring opening of $[Cr(H_2O)_4(OOCCH(CH_3)S)]^+$.

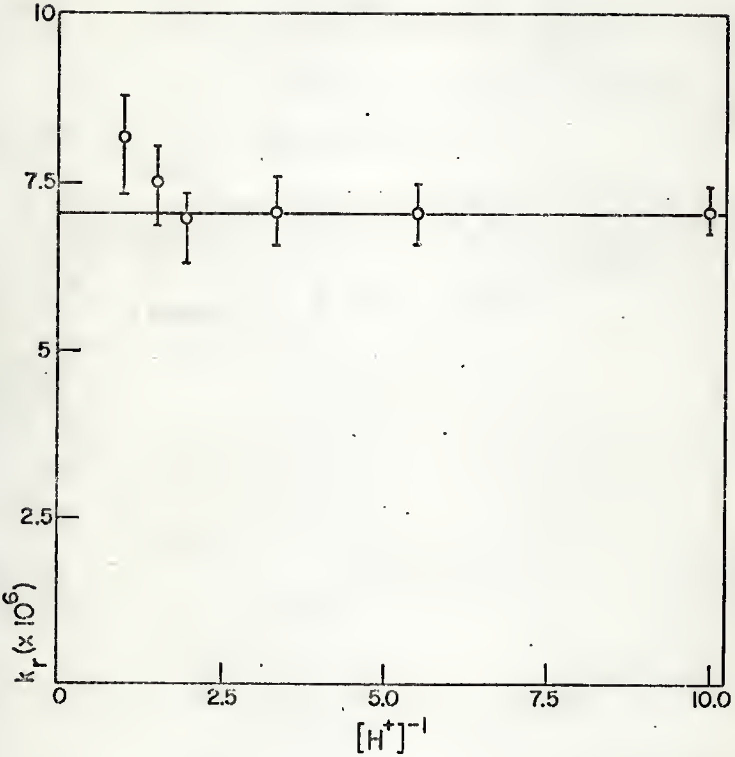


Figure 7. Acid independence of ring closure of $[Cr(H_2O)_5(OOCCH(CH_3)SH)]^{2+}$.

When excess chromium(II) was used in the initial reaction of chromium(II) with $[Co(en)_2(OOCCH(CH_3)S)]^+$, no subsequent spectral change indicative of the conversion of I to II was observable on the stopped-flow instrument. Duplication of the conditions for product studies yielded the chelated 2-mercaptopropionato-chromium(III) complex in virtually stoichiometric amounts. These observations indicate that there is, in the presence of excess chromium(II), another reaction of the mercaptide-bound pendant intermediate. This is most likely a second oxidation-reduction reaction in which chromium(II) reacts with the monodentate chromium(III) product initially formed to produce chelated chromium(III) product and regenerate chromium(II). In view of the latter product, this can be considered as a chromium(II)-catalyzed chelate ring closure. Similar observation have been made for the analogous 2-mercaptoacetato chromium(III) and maleato chromium(III) systems, respectively.[10,30]

Lactate as Ligand

The lactate ligand system was included in this study primarily for comparative purposes in the redox reations with attention focused primarily on the sulfur analogue. As such, detail of investigation into the chromium(III)-lactate system is less than that previously described for the 2-mercaptopropionate system, but the experimental results obtained suggest that future exploration of the oxygen system merits consideration. The following observations delineate the limits of our investigation.

As previously discussed, the monodentate alkoxide-bound chromium(III) species, $[Cr(H_2O)_5(OCH(CH_3)COOH)]^{2+}$, has not been experimentally observable as a product of the Cr(II)-$[Co(en)_2(OOCCH(CH_3)O)]^+$ reaction at high pH and of the path inverse in acid at low pH. The observable products, identified by chromium analysis, ion exchange chromotography and spectral studies as $[Cr(H_2O)_5(OOCCH(CH_3)OH)]^{2+}$ and $[Cr(H_2O)_4(OOCCH(CH_3)O)]^+$, arise in varying ratios which are dependent on the acidity conditions. Further, the isolated species are interconvertible as a function of the acidity.

Only the blue, +2 ion is produced under conditions comparable to the following: $[H^+] = 0.100$ M, $[Co(III)] = 0.10 - 0.010$ M with chromium(II) ion in excess, stoichiometric or deficient amounts. The ion-exchanged +2 ion, maintained throughout at pH = 1, yielded the following spectral parameters: $[\lambda(\epsilon)$: 568(26.8), 413(33.2)]. Dropwise addition of 1.0 M NaOH to this solution to 2.8 = pH = 3.6 (*via* pH meter) produced a pink-orange species whose visible spectrum had the following characteristics: $[\lambda(\epsilon)$: 548(31 ± 1.5, 438(38 ± 1.6)]. Reacidification of the solution to pH = 1 regenerated the blue species originally obtained, *viz*., $[\lambda(\epsilon)$: 568(25 ± 1), 413(34 ± 1)]. If, instead of using an eluent of pH = 1, a neutral eluent is used, the blue ion elutes as a +2 ion but turns pink immediately on coming off the column. The pH of this solution was found to be 2.8 and the visible spectrum was identical to that previously characterized as the $[Cr(H_2O)_4(OOCCH(CH_3)O)]^+$ ion. Acidification of this solution to pH = 1 regenerates the previously described $[Cr(H_2O)_5(OOCCH(CH_3)OH)]^{2+}$ species as identified by its visible spectrum.

In order to test the possibility that the conversions were simply due to proton transfer, which should be extremely rapid, stopped-flow kinetic runs were carried out. A solution of the +1 ion, generated by conversion of the +2 ion through appropriate adjustment of the pH to 3.0, was reacted separately with equal volumes of 0.100 M and 0.200 M $HClO_4$ (μ = 0.25 M ($HClO_4$--$LiClO_4$)). Concentrations after mixing were $[Cr(III)] = 1.0 \times 10^{-3}$ M, $[H^+]$ = 0.050 M and 0.100 M, respectively. Spectrophotometric monitoring was at 438 nm, a maximum for the chelate species. A plot of $\log(A_t - A_\infty)$ vs t gave a first-order rate constant of $k_{obs} = 3.2 \times 10^{-2}$ sec^{-1} for both acidities, showing the overall rate process to be measurable. Thus, simple proton transfer appears excluded.

The lower limit of acidity used for the redox reaction (4.0×10^{-4} M) was dictated by the release of two moles of ethylenediamine per mole of oxidant. Upon reaction the pH increases due to the consumption of protons by the amine functions thereby introducing the hazard of metal hydroxide precipitation. Using this initial acidity with stoichiometric amounts of chromium(II) ion and cobalt(III) complex results, upon cation exchange separation of the products using neutral eluent, in isolation of a +1 and a +2 ion in the molar ratio 2:1. The ions were characterized spectrally as the $[Cr(H_2O)_4(OOCCH(CH_3)O)]^+$ and $[Cr(H_2O)_5(OOCCH(CH_3)OH)]^{2+}$ species. Again variation in acidity produced interconversion of the ions as previously observed.

Methylthioacetate as Ligand

The relationship between this ligand and the mercaptoacetate ligand, of which it is a derivative, and the similarity of their cobalt(III) complexes invites a comparison of the behavior of the chromium(III) products. Relative to the previous results with mercaptoacetate, any differences would be directly ascribable to the transformation of the mercaptide function to a thioether function.

The only isolable product of the initial oxidation-reduction reaction in the acidity range 0.100 M $\geq [H^+] \geq$ 0.010 M and with chromium(II) in excess, stoichiometric or deficient amounts was the carboxylate-bound chromium(III) product $[Cr(H_2O)_5(OOCCH_2SCH_3)]^{2+}$, the characterization of which has previously been described. The ion underwent no reaction of interest other than hydrolysis to the $[Cr(H_2O)_6]^{3+}$ species; therefore no further work with this ion was undertaken.

By employing techniques analogous to those used for the thiolactate complex, the author hoped to be able to discern formation of a thioether-bound intermediate, thus confirming the bridging ligand as the thioether rather than carbonyl oxygen. Reactions were performed using the all-glass mixing apparatus and the Cary 14 instrument. The reactions were monitored at 530 nm, an absorbance maximum for the chromium(III) chelate complex (by analogy with similar complexes, Table III), and at 270 nm, the spectral region of greatest difference in molar absorptivities for the sulfur-bound species relative to the carboxylate-bound monodentate chromium(III) product. The respective experimental conditions were as follows: 530 nm; $[Co(III)] = 5.10 \times 10^{-4}$ M, $[Cr(II)] = 4.7 \times 10^{-4}$ M, $[H^+] =$ 0.100 M and $\mu = 1.00$ M ($HClO_4LiClO_4$), 270 nm; $[Co(III)] = 2.58 \times 10^{-4}$ M, $[Cr(II)] = 2.35 \times 10^{-4}$ M, $[H^+] = 0.100$ M and $\mu = 1.00$ M ($HClO_4$--$LiClO_4$). In both cases a rapid decrease in absorbance corresponding to 90% reaction for the oxidation-reduction was followed by a slow, small decrease in absorbance. The plot of $\log (A_t - A_\infty)$ vs t was characteristic of two consecutive first-order reactions subsequent to the initial oxidation-reduction. A plot of

$$\log \frac{(\frac{b}{a} - 1)A_o - (\frac{b}{a})A_\infty + A_t}{A_t - A_\infty} \quad \underline{vs} \quad \text{time}$$

for the initial rapid decrease in absorbance was characteristic of a second-order reaction corresponding to reaction of $[Co(en)_2(OOCCH_2SCH_3)]^{2+}$ with Cr(II).

The subsequent consecutive first-order reactions can be understood in terms of a two-step mechanism consisting of: (1) closure of a first-formed sulfur-bound monodentate chromium(III) product to yield the chelate $[Cr(H_2O)_4(OOCCH_2SCH_3)]^{2+}$ followed by; (2) opening of the chelate ring to yield the carboxylate-bound monodentate $[Cr(H_2O)_5(OOCCH_2SCH_3)]^{2+}$ species. The subsequent first-order reactions observed can be rationalized only with great difficulty if redox bridging is postulated to proceed via carbonyl oxygen.

Glycinate as Ligand

The inclusion of this ligand system in the present study was, as in the lactate case, primarily for purposes of comparison in interpreting reactivity patterns. As such, detailed investigative work into the products of the reaction of chromium(II) with $[Co(en)_2(OOCCH_2NH_2)]^{2+}$ was not carried to the extent of the 2-mercaptopropionate system. As will be discussed below, limitations imposed by the system itself hinder complete work, but certain salient features of the chromium(III) glycinate product were accessible.

In the range of acidity used (0.100 M $\geq [H^+] \geq$ 0.0100 M) the reaction of $[Co(en)_2(OOCCH_2NH_2)]^{2+}$ with chromium(II) used in excess, stoichiometric, or deficient amounts, the only isolable product was characterized as the ion $[Cr(H_2O)_5(OOCCH_2NH_3)]^{3+}$ with spectral parameters as follows: $[\lambda(\epsilon)$: 573(22 ± 1.1), 411(23.0 ± 1.6)]. The ion was eluted from a cation exchange column in the lithium form with 1.0 M $LiClO_4$. The pH of the eluted solution was found to be 3.5 ± 0.1. Upon addition of 1.0 M NaOH solution to the product solution until pH = 4.5 ± 0.1, the solution color changed immediately from blue to green, but yielded virtually the same visible spectrum as the original solution. After several days the color had changed to a red-violet and separation was effected using ion exchange techniques. A fraction presumed to contain a +2 ion was collected which exhibited the following visible spectrum: $[\lambda(\epsilon)$: 55(38.0 ± 5), 420(41 ± 6)] (pH = 4.5). The large error limits for the molar extinction coefficients are a result of the dilute solutions (10^{-4} M) necessarily employed. From the rather high values for the coefficients in comparison with monodentate carboxylate-bound chromium(III) species (Table II), the ion is presumed to be $[Cr(H_2O)_4(OOCCH_2NH_2)]^{2+}$. The important features are that a 1:1 glycine-chromium(III) product can be isolated from the appropriate pH, undergo a subsequent reaction to yield, in part a chromium(III)-glycine chelate complex.

DISCUSSION

The primary objective of this research was to better define the influence which coordinated sulfur functions have on the reactivity of metal complexes in oxidation-reduction reactions. Conclusions relating to this objective will be discussed first.

Reduction of the Co(III) Complexes by Chromium(II)

All redox reactions between the cobalt(III) complexes and chromium(II) were demonstrated to proceed by inner-sphere pathways through product analysis.

In attempting to understand the rate and activation energy data to be presented, it is convenient to describe the net process for an inner-sphere electron transfer reaction as series of steps[15,44] represented by the following equations (for clarity, only the bridging ligand is represented):

$$\mathrm{Co(II)X + Cr(II)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Co(III)\text{-}X\text{-}Cr(II)} \qquad K_1 \qquad (14)$$

$$\mathrm{Co(III)\text{-}X\text{-}Cr(II)} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [\mathrm{Co(III)\text{-}X\text{-}Cr(II)}]^* \qquad K_2 \qquad (15)$$

$$[\mathrm{Co(III)\text{-}X\text{-}Cr(II)}]^* \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [\mathrm{Co(II)\text{-}X\text{-}Cr(III)}]^* \qquad (16)$$

$$[Co(II)\text{-}X\text{-}Cr(III)]^* \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} Co(II)\text{-}X\text{-}Cr(III) \qquad (17)$$

$$Co(II)\text{-}X\text{-}Cr(III) \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} Co(II) + X\text{-}Cr(III). \qquad (18)$$

Equation (1) represents the substitution equilibrium between the reactants and bridged precursor complex which can rearrange to the activated complex (2). Electron transfer is represented by equation (3) while equations (4) and (5) represent subsequent deactivation of the successor complex and decay to products, respectively.

The rate of formation of the precursor complex can in certain cases be rate determining. If the collision rate for the positively charged complexes is taken to be 10^9 $\underline{M}^{-1}$ sec^{-1}, the lifetimes of the resulting outer-sphere encounter complexes estimated as 10^{-11} - 10^{-12} sec, and the rate of exchange of a water which is coordinated to chromium(II) and proximate to the bridging ligand is 10^9 - 10^{10} sec^{-1},[7a,b] an estimate of 10^7 $\underline{M}^{-1}$ sec^{-1} is obtained for k_1.[7c] Should k_1 not be the rate determining step, the stability of the precursor complex becomes important as an equilibrium prior to the rate-determining step, formation of the activated complex. In this case the free energy of activation can be expressed as $\Delta G^{\ddagger} = -RT \ln(K_1K_2)$. This enables a discussion of the reactivities in terms of steps (1) and (2) whether or not they are actually isolated in time.

This model provides a basis for the discussion of the reactivity parameters obtained in this study together with previous results which are included for purposes of comparison (Table XII).

TABLE XII

Reactivity Parameters for the Reaction of Some Cobalt(III) Complexes with Chromium(II)

Entry	Species	Mechanism	$k_{Cr(II)}$ $\underline{M}^{-1}$ sec^{-1}	$\Delta H^{\ddagger}$ Kcal mole^{1-}	$\Delta S^{\ddagger}$ eu	$\Delta G^{\ddagger}$ Kcal mole^{-1}	Ref.
1	$[Co(NH_3)_5(OOCH)]^{2+}$	i(COO)	7.2	8.3	-27	16	15
2	$[Co(NH_3)_5(OOCCH_3)]^{2+}$	i(COO)	0.35	8.2	-33	20	15
3	$[Co(NH_3)_5(OOCC(CH_3)_3)]^{2+}$	i(COO)	0.0096	11.1	-31	20	15
4	$[Co(NH_3)_5(OOCCH_2NH_3)]^{3+}$	i(COO)	0.06	7.7	-38	19	15
5	$[Co(NH_3)_5(OOCCH_2OH)]^{2+}$	i(COO)	3.1	9.0	-26	17	35
6	$[Co(NH_3)_5(OOCCH(CH_3)OH)]^{2+}$	i(COO)	6.65	--	--	--	15
7	$[Co(NH_3)_5(OOCC(CH_3)_2OH)]^{2+}$	i(COO)	11.5	9.1	-24	16	35
8	$[Co(en)_2(OOCCH_2NH_2)]^{2+}$	i(COO)	2.22	8.8	-27.4	17.0	c
9	$[Co(en)_2(OOCCH_2SCH_3)]^{2+}$	i(S)	274	8.5	-18.9	11.2	c
10	$[Co(en)_2(NH_2CH_2CH_2SCH_3)]^{3+}$	i(S) ?	0.38	5.4	-42.4	18.0	46
11	cis-$[Co(en)_2(OOCH)_2]^{+}$	i(COO)	50	7.9	-25	15.4	d
12	$[Co(en)_2(OOCCH_2O)]^{+}$	i(O)	1.9×10^3	(2.2)	(-36)	(13)	10
13	$[Co(en)_2(OCH_2CH_2NH_2)]^{2+}$	i(O)	935	5.1	-28	13.6	46
14	$[Co(en)_2(OOCCH_2S)]^{+}$ e	i(S)	6.4×10^6	(1.1)est	(-24)est	(6.9)est	10
15	$[Co(en)_2(NH_2CH_2CH_2S)]^{2+}$	i(S)	3.5×10^4	7.3	-13.3	11.2	46
16	$[Co(NH_3)_5(py)]^{3+}$	o	0.0043	9.8	-36	21	f
17	$[Co(NH_3)_5(nicotinamide)]^{3+}$	i	0.033	10.2	-31	20	g
	(pyridine-N-bound)	o	0.014	9.2	-36	20	g

TABLE XII continued

Entry	Species	Mechanism	$k_{Cr(II)}$ M^{-1} sec^{-1}	$\Delta H^{\ddagger}$ Kcal mole^{-1}	$\Delta S^{\ddagger}$ eu	$\Delta G^{\ddagger}$ Kcal mole^{-1}	Ref.
18	$[Co(NH_3)_5(4\text{-pyridone})]^{3+}$	i	0.014	--	--	--	h
	(oxygen-bound)	o	0.0096	--	--	--	h
19	$[Co(NH_3)_5(OC(NH_2)_2)]^{3+}$	o ?	0.019	10.6	-31	20	i
20	$[Co(NH_3)_5(NCNC(NH_2)_2)]^{3+}$	o ?	0.029	8.3	-37	19	i
21	$[Co(en)_2(OOCCH(CH_3)O)]^{+}$	i(O)	52	(2.3)est	(-43)est	(15)est	c
22	$[Co(en)_2(OOCCH(CH_3)S)]^{+}$ [e]	i(S)	1.55 x 10^5	1.1	-31.1	10.4	c
23	cis-$[Co(en)_2(Cl)(H_2O)]^{2+}$ [e]	i(Cl)	3.8 x 10^5	1	-29	9.8	44c
24	cis-$[Co(en)_2(F)(H_2O)]^{2+}$ [e]	i(F)	1.4 x 10^5	0.0	-34	10.4	44c
25	$[Co(NH_3)_5(OH)]^{2+}$	i(O)	1.5 x 10^5	4.6	-18	10	j

[a] μ = 1.00 M. [b] 25.0°C. [c] This work. [d] J.F. Ward and A. Haim, J. Amer. Chem. Soc., 92, 475(1970). [e] μ = 0.10 M. [f] R. G. Linck in "Reaction Mechanisms in Inorganic Chemistry," M.L. Tobe, Ed., Medical and Technical Publishing Co. Ltd., London, In press. [g] F. Nordmeyer and H. Taube, J. Amer. Chem. Soc., 90, 1163(1968). [h] E. S. Gould, J. Amer. Chem. Soc., 90, 1740(1968). [i] E. J. Balahina and R. B. Jordan, J. Amer. Chem. Soc., 93, 625(1971). [j] A. Zwickel and H. Taube, J. Amer. Chem. Soc., 81. 1288(1959).

For clarity the results will be discussed according to the sequence of bridging functions (1) chelated carboxylate, (2) chelated thioether (3) chelated thiolate and alkoxide. The order of entries in Table XII is that in which they are encountered in this discussion.

Chelated Carboxylate as a Bridging Function

All the complexes studied contained as potential bridging functions coordinated carboxylate groups in bidentate ligands with the other donor function also coordinated to the same metal center. This situation represents a departure from previous studies in which simple monodentate carboxylate ligands were examined or in which a potentially chelating donor function remained pendant from the carboxylated metal. It was, therefore, deemed essential to establish any distinctions in bridging efficiency between the carboxylate group of a chelate and those previously studied. For this reason the reaction of $[Co(en)_2(OOCCH_2NH_2)]^{2+}$ with chromium(II) was investigated.

Entries 1-7 of Table XII summarize prior experimental results for the types of carboxylate coordination previously studied. The acetato complex, entry 2, can be taken as the prototype. The more rapid rate of reduction observed for the formato complex, entry 1, resides in the entopy component and can be attributed to a diminished steric restriction[15] which is expected to be concentrated in a greater stability of the precursor complex, K_1. While the rate of the more sterically hindered iso-butyrato complex, entry 3, is diminished as expected, the source of this diminution is found unexpectedly in the enthalpy of activation, a result not understood by this author. The diminished rate for the pendant glycinato complex, entry 4, is attributable to the entropy difference, a logical consequence of the increased charge.[15] Entries 5, 6 and 7 are for complexes with pendant functions which can chelate the chromium(II) reductant. The expected greater stability of the precursor complex and enhanced rates are reflected in more favorable entropy contributions.

In this context the enhanced rate for the chelated glycinato complex, entry 8, appears easily understood. The acceleration finds its source in the entropy term. This is ascribed to a greater stability of the precursor complex when the carbonyl function to which chromium(II) most probably binds[15] is held in a more accessible position as a result of chelation by the amine function. This effect is expected to extend, with allowances for variations in charge type, to other chelated carboxylate ligands, thereby fulfilling one objective of this research.

Chelated Thioether as a Bridging Function

For the important case of thioether coordination in $[Co(en)_2(OOCCH_2SCH_3)]^{2+}$, entry 9, it was not possible to define the bridging function through isolation of the chromium(III) product which was always found to be $[Cr(H_2O)_5(OOCCH_2SCH_3)]^{2+}$. While this result appears to indicate carboxylate bridging it is important to consider the initial product of the alternative sulfur-bridged path,

$[Cr(H_2O)_5(CH_3SCH_2COOH)]^{3+}$. Such a consideration is mandatory in view of a rate substatially greater than that found as typical for carboxylate bridging even in a chelated example of the same charge type, vide supra. Further, previous research[45] suggests that chelate closure of the alternative product to yield $[Cr(H_2O)_4(CH_3SCH_2COO)]^{2+}$ could occur in times shorter than those required for isolation at the acidity level (0.100 $\underline{M}$) of our experiments. A relatively rapid hydrolysis of the chromium-thioether bond, which would not be surprising, would lead to our product observations.

In this context it should be noted that the relatively rapid redox rate observed arises exclusively from an entropy contribution which is ~12 eu more favorable than for any previously studied carboxylato-bridged reaction lacking a pendant donor function. Further, the absorbency changes at 530 nm and 270 nm reveal a sequence of three steps which cannot be ascribed to carboxylate bridging, a mechanism which should result in a single-step absorbency change. However, the two substitutional processes previously described for $[Cr(H_2O)_5(CH_3SCH_2COOH)]^{3+}$ could account for two absorbency changes subsequent to the redox step. These results are taken as indicative of bridging via the thioether function. If this interpretation is correct, the inner-sphere reactivity bestowed by a coordinated thioether is one of very few examples lying intermediate between that bestowed by very efficient bridging ligands, e.g. the halides and thiolates, and by the rather mediocre bridging ligands, e.g. water and carboxylate. Thus, a second major objective of this study seems fulfilled.

A detailed discussion of the reactions of the $[Co(en)_2(CH_3SCH_2CH_2NH_2)]^{3+}$ complex, entry 10, is appropriately deferred to another thesis.[46] However, its greater diminished reactivity is attributable to a substantial decrease in the entropy term while the enthalpy actually contributes in the opposite direction. In fact, its reactivity parameters, in comparison with those for the complex described here, are decidedly at variance with those anticipated for an inner-sphere reaction in which the non-bridging function _cis_ to the bridging ligand has been changed from carboxylate to amine. Such a change results in little variation in all parameters for one comparison, entry 11 _vs_ entry 1, and little variation in the observed rate for another, entry 12 _vs_ entry 13. A somewhat different pattern emerges for two other inner-sphere reactions entailing a similar variation of the _cis_ non-bridging function, entries 14 and 15. The reasons for this different pattern are not yet understood. However, if the more rapid rate of reduction for the $[Co(en)_2(OOCCH_2S)]^{2+}$ complex is ascribed to enthalpic and entropic variations similar to those used for the thioether comparison a value for the entropy of activation is obtained which seems unrealistically high. Thus, a different comparative pattern from those previously observed for consistently inner-sphere reactions is evident. The results reported here may prove useful in assigning the reduction of $[Co(en)_2(CH_3SCH_2CH_2NH_2)]^{3+}$ to the outer-sphere category. The activation parameters are in substantial agreement for other outer-sphere reductions involving +3 ions, entries 16-20, although this, in itself, is not diagnostic of the mechanism.

Thiolate and Alkoxide as Bridging Functions

In the pioneering research in this area, Lane found a reactivity for coordinated thiolate as a bridging function which exceeded that for a comparably coordinated alkoxide by a factor of >3,000.[10] Three possible reasons for this enhanced reactivity were presented: (1) a greater stability of the precursor complex with the thiolate ligand arising from the greater steric accessibility of the sulfur atom, (2) a cobalt-sulfur bond which is weaker than the cobalt-oxygen bond, thereby requiring less enthalpy for activation of the precursor complex, (3) a possibly greater sigma covalency in the cobalt-sulfur bond which might contribute to an enhanced probability for electron transfer. No distinction was possible between the relative contributions to the reactivity from these sources.

The initial phases of this study were directed toward providing such a distinction. Space-filling models suggested that the methylene hydrogens on the carbon atom adjacent to the coordinated chalcogenide would inhibit precursor complex formation with $[Cr(H_2O)_5]^{2+}$ to a greater extent for alkoxide than for the larger thiolate sulfur. According to this view, it was felt that substitution of one or two methyl groups on this carbon atom would diminish the rate of reduction for both complexes via a steric effect without drastically altering the electronic contributions. (Unfortunately attempts to prepare the dimethyl derivative were unsuccessful, but the monomethyl derivative proved to be synthetically accessible.) It was naively assumed that the reactivity of the thiolate complex would be less sensitive to this change than the complex with a smaller, less accessible oxygen-bridging atom. Finally, if the expected diminutions in rates actually materialized it was hoped that a determination and comparison of the activation parameters would be possible.

The anticipated decrease in the rate of reduction was, in fact, observed, as a comparison of entries 12 and 21, 14 and 22 indicates. Surprisingly, the factor by which the rate is decreased is ~1/40 for both the alkoxide and thiolate complexes. This implies that any greater anticipated steric susceptibility to inhibition for the alkoxide function compared to that of the thiolate is not developed by monomethyl substitution. For both complexes the decrease in the accessibility of the bridging atom would, in the absence of sufficient activation parameter data, appear to be comparable implying a highly directional approach for the $[Cr(H_2O)_5]^{2+}$ residue (i.e., the methyl function exerts a restrictive influence but can be comparably avoided in both cases).

In the case of the mercaptopropionate complex it was possible, as the anticipated result of the decrease in rate, to measure the activation parameters. The enthalpy of activation of 1.1 kcal/mole reflects an unusually small resistance to reaction from this factor. The reason for the difference in this parameter in the reduction of the mercaptoethylamine example, the only other case for which it has been determined, is not presently understood. The latter complex may be anomalous with regard to the enthalpy contribution. Its anomalous absorption spectrum in the visible region suggests something unusual in its electronic configuration.[47] Even if this were not the case certain differences should be recognized in the two ligands. The mercaptopropionate ligand possesses an sp^2 carbon in the chelate skeleton whereas the mercptoethylamine has only sp^3 carbon atoms. This difference could result in different conformations for the two chelated ligands. The consequences for the activation parameters of such variations in chelated ligands is essentially unexplored. Further speculation is best postponed until more data are available.

The observed entropy of activation for the mercaptopropionate complex seems remarkably positive for a species with a methyl group and a hydrogen atom on a carbon atom bound to the bridging atom and further constricted by the chelation of the ligand. In fact, the steric restrictions appear to leave the sulfur as accessible as the halide-bridging ligand in cis-$[Co(en)_2(Cl)(H_2O)]^{2+}$ and cis-$[Co(en)_2(F)(H_2O)]^{2+}$ and, in spite of the methyl substitution, less restricted than the alkoxide oxygen of the unsubstituted glycollate complex, *vide infra*. These entropy trends are taken as indicative of a uniqueness of the large coordinated sulfur atom in remaining sterically accessible in spite of rather bulky substitutions.

The activation parameters reported in Table XII for the glycollate complex, entry 12, are to be regarded as tentative and subject to confirmation. Nevertheless, they appear reasonable in that $\Delta H^{\ddagger}$ lies intermediate between that for a mercaptide bridge in a comparable environment, entry 22 (compare also entries 23 and 24), and that reported for $[Co(NH_3)_5OH]^{2+}$, which should have a higher $\Delta H^{\ddagger}$ as the result of the change in non-bridging ligands; compare entries 1 and 11. The value for $\Delta S^{\ddagger}$ seems appropriate.

The discrepancy between the tentative value for $\Delta H^{\ddagger}$ of 2.2 kcal/mole and the 5.1 kcal/mole observed for the reduction of $[Co(en)_2(OCH_2CH_2NH_2)]^{2+}$ may arise from an enthalpic anomaly for the latter similar to that suspected for the $[Co(en)_2(SCH_2CH_2NH_2)]^{2+}$ analogue. If these are viewed as anomalous activation enthalpies it seems possible to obtain tentative estimates for four unknown activation parameters which appear reasonable, internally consistent and in satisfactory comparison in the entropy term with the measured values for the anomalous complexes.

The estimation proceeds as follows. Since the effect of methyl substitution on the adjacent carbon is primary steric and is comparable for both alkoxide and thiolate complexes, it seems reasonable to attribute the rate of decrease to the entropy term. If the value of 1.1 kcal/mole for $\Delta H^{\ddagger}$ in the mercaptopropionate reaction is used for the mercaptoacetate reaction a value for $\Delta S^{\ddagger}$ of -25 eu is obtained. The increase from -31 eu seems reasonable for the loss of the methyl substituent. Further, the increase from -36 eu for the oxygen analogue is comparable to the 14.7 eu increase observed for a similar change in going from $[Co(en)_2(OCH_2CH_2NH_2)]^{2+}$ to $[Co(en)_2(SCH_2CH_2NH_2)]^{2+}$. Proceeding in the reverse direction, $\Delta H^{\ddagger}$ of 2.2 kcal/mole for the glycollate complex is assumed for the lactate complex. This yields a value of -43 eu for $\Delta S^{\ddagger}$ which is again ~12 eu more negative than for the sulfur analogue and ~7 eu more negative than for reaction with the complex not substituted by a methyl group.

To the extent that these estimates are reasonable the following tentative conclusions for the inner-sphere reaction can be drawn. (1) The carboxylate-chalcogenide chelates with an sp^2 carbon atom in the five-membered chelate ring bestow an entropic barrier to activation which is about 8-10 eu more negativo than for the amine-chalcogenide chelates with no sp^2 carbon. This difference seems reasonable in view of possible conformational differences mentioned earlier. (2) The substitution of a methyl function on the carbon adjacent to the chalcogenide atom in the carboxylate-chalcogenide chelate increases the entropic barrier to activation by 6-7 eu. (3) The substitution of sulfur for oxygen in otherwise analogous alkoxide complexes lowers the entropic barrier by 12-15 eu while the enthalpy decrease contributes about one order of magnitude (1.4 kcal/mole) to the reactivity. Thus, at least for the carboxylate-chalcogenide ligands, the enhanced reactivity on substituting sulfur for oxygen seems to derive about 35% from a lowering of $\Delta H^{\ddagger}$ and about 65% from a more positive $\Delta S^{\ddagger}$. Therefore, the steric component associated with the larger sulfur atom appears to be larger than the electronic contribution to the observed enhancements. Thus, within the limitations expressed earlier, a third objective of the research seems reasonably fulfilled. In this regard we wish to acknowledge our indebtedness to the research of Robert H. Lane and Michael J. Gilroy without which the necessary comparisons would not have been available.

Substitution Reactions at Chromium(III)

Chromium(III)-Mercaptopropionate System

As previously described, the substitution behavior of the

2-mercaptopropionate-chromium(III) product may be represented by the following steps:

$$\underset{\text{I}}{[\mathrm{Cr(H_2O)_5(SCH(CH_3)COOH)}]^{2+}} \xrightarrow{k} \underset{\text{II}}{[\mathrm{Cr(H_2O)_4(SCH(CH_3)COOH)}]^{+}}$$

$$[\mathrm{Cr(H_2O)_4(SCH(CH_3)COO)}]^{+} + \mathrm{H}^{+} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} [\mathrm{Cr(H_2O)_5(OOCCH(CH_3)SH)}]^{2+}$$

$k = (1.0 + 2.6\,[\mathrm{H}^{+}]) \times 10^{-2}$ ($\underline{M}$ and sec)

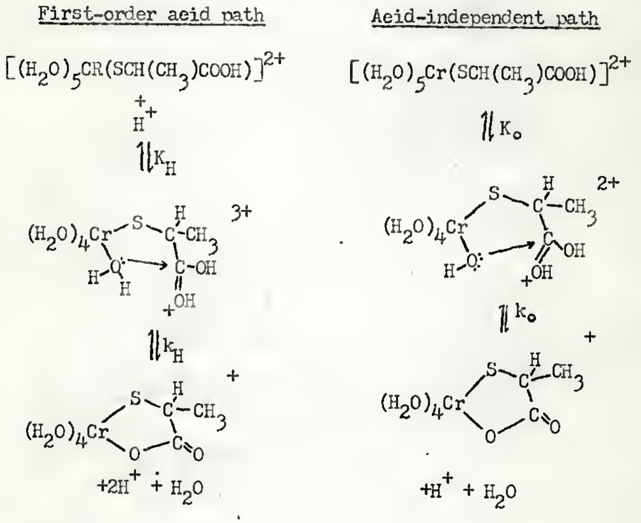
$k_f = (7.31\,[\mathrm{H}^{+}]) \times 10^{-5}$ ($\underline{M}$ and sec)

$k_r = 7.10 \times 10^{-6}$ ($\underline{M}$ and sec)

These are to be compared to the analogous k, k_f and k_r for mercaptoacetate[10] and for malonate:[48]

Mercaptoacetate as ligand;	Malonate as ligand;
$k = (5.6 + 13\,[\mathrm{H}^{+}]) \times 10^{-3}$	$k = (4.0 + 22\,[\mathrm{H}^{+}]) \times 10^{-6}$
$k_f = (73\,[\mathrm{H}^{+}] + 0.6) \times 10^{-6}$	
$k_r = (68 + 0.8\,[\mathrm{H}^{+}]^{-1}) \times 10^{-7}$	

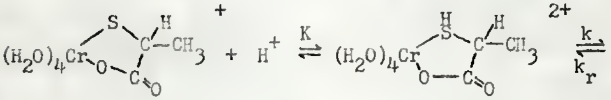
The initial chelate ring closure will be considered first. In the first report of an analogous chelate ring closure by carboxylate which follows a rate law of this form,[48] the proposition was advanced that the acid-dependent ring closure involved substitution of a coordinated water at the carbon of a protonated carbonyl function. The possibility of a similar substitution by coordinated hydroxide in the acid-independent path was recognized but, understandably, not strongly advocated in view of the alternative possibility of substitution at chromium. Similar conclusions were reached in the case of the mercaptoacetate where the ~1,000-fold enhancement in rate was primarily attributed to the higher steric feasibility for closure of the five-membered chelate ring than for the six-membered ring of the malonate system. Some contribution arising from an enhanced nucleophilicity of water or hydroxide cis to the mercaptide donor function was also recognized.[10] These schemes are considered to apply to the 2-mercaptopropionate system and are outlined in the following diagrams:



$k_H K_H = 2.6 \times 10^{-2}$ $\qquad$ $k_\circ K_\circ = 1.0 \times 10^{-2}$

The essentially unchanged ratio for the two paths at constant acidity in all three systems lends some credence to the proposed similarity in mechanism as opposed to substitution at chromium in the acid-independent path. Further, the similar enhancement **observed** for the 2-mercaptopropionate system in both paths over the mercaptoacetate system is that anticipated for a slightly enhanced basicity of the carbonyl oxygen arising from methyl substitution.

A comparison of the data for the ring opening and closure of the chelate complex at the metal-sulfur bond provides the most striking deffcrence between the two mercaptide ligands. For the methyl-substituted ligand no acid-independent term for k_f (acid-dependent for k_r) was observed whereas the mercaptoacetate system has a term. A discussion of possible reasons for this will be presented later. The acid-dependent term for k_f can be rationalized by the following mechanism:



$$[(H_2O)_5Cr(OOCCH(CH_3)SH)]^{2+}$$

$$k_f = Kk$$

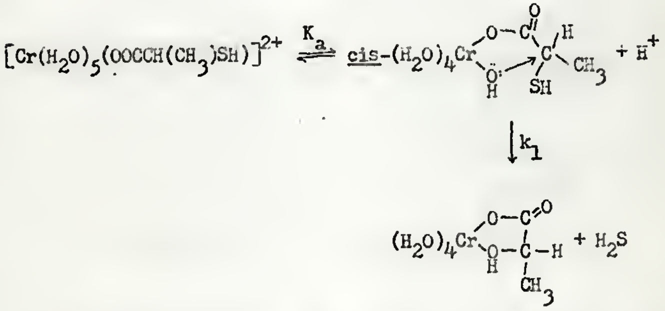
Such a mechanism has been proposed for the analogous path in the mercaptoacetate case and from the similarity in the rate laws is similarly reasonable here. On the basis of inductive effect, it is somewhat surprising that k_f is not larger due to increased basicity of the mercaptide. However, a slightly larger K might be compensated by a comparably smaller k. Any variation is expected to be small in view of the fact that the equilibrium constant for the dechelation process ($10.5 \pm .12$) is experimentally indistinguishable from that for analogous process with mercaptoacetate as ligand (10.3 ± 1.3)[10] thus reflecting little change in the sulfur function.

The essential identity in rate of this process to the analogous path in the mercaptoacetate system (7.1×10^{-6} vs 6.8×10^{-6}) virtually ensures that the mechanisms, as expected, are the same.

Thus the arguments presented for that system are applicable here and will not be repeated in detail. Thus it seems highly probable that bond-making is more important than bond-breaking for both forward and reverse processes. No evidence exists to suggest that the acid-catalyzed metal-sulfur cleavage differs dramatically from the analogous metal-fluoride cleavage in $[Cr(H_2O)_5F]^{2+}$ ($k = (1.38 \times 10^{-8})\,[H^+]$)[49a] except in the greater basicity of the coordinated mercaptide. Further, the rate enhancement for chelate closure by the mercaptan function by factors of 30-250 over the rates for monodentate ligation of $[Cr(H_2O)_6]^{3+}$ by HF($k = 2.2 \times 10^{-7}$) of HN_3 ($k = 2.8 \times 10^{-8}$)[49] appears primarily attributable to a "chelate effect" in which the pendant mercaptan function can better trap a vacated coordination site rather than to a higher associative reactivity.

With regard to the lack of an acid-independent term in k_f (acid-dependent for k_r) for the mercaptopropionate system in comparison to its presence in the mercaptoacetate system, it should be noted that by necessity our experiments were carried out over a higher range of acidity (0.10 M - 1.0 M) than that for the mercaptoacetate case (0.010 M - 0.20 M). Thus, within probable experimental error, the zero intercept for the k_f *vs* $[H^+]$ plot is likely to be indistinguishable from the anticipated 0.6×10^{-6} previously detected. Further, a line of positive slope drawn through the error limits of our most reliable experiments (<0.5 M) in the k_r *vs* $[H^+]$ plot would allow for a $0.1 \times 10^{-6}\,[H^+]$ contribution to k_r while requiring only a small revision to 6.1×10^{-6} in the acid-independent term. In view of the similarities of the ligands it seems likely that this path would disappear and more reasonable that, under the conditions accessible to us, it is undetectable.

The fact that the acidity range previously studied with a very similar ligand-complex system was not accessible with 2-mercaptopropionate is of obvious interest. Equilibration experiments below 0.10 M acid were irreproducible and the odor of H_2S was clearly detectable. A previous study of cis-$[Co(en)_2(OH)NH_2CH_2CH_2Br)]^{2+}$ revealed a lysis of the methylene-bromine bond by attack of coordinated hydroxide on the saturated carbon atom to produce $[Co(en)_2NH_2CH_2CH_2O)]^{2+}$ and Br^-.[37] Thus, the most obvious explanation of our results invokes a comparable lysis of the carbon-sulfur bond.



Consideration of the S_N2 mechanism for the attack of coordinated hydroxide on the saturated carbon suggests that for both steric and electronic reasons the presence of the methyl group on the carbon atom of interest should decrease the tendency towards direct attack.[50] Alternate mechanisms, however, can be defended only with difficulty relative to the observed product behavior. Until further planned work on this system is accomplished no definite conclusion as to the reason for the reactivity of the complex can be reached.

Chromium(III)-Lactate System

For the lactato and glycollato complexes of chromium(III), the lack of extensive data precludes a discussion in the detail afforded the mercaptide systems. For the reaction

$$[Cr(H_2O)_4(OOCCH(R)O)]^+ \underset{k_r}{\overset{k_f}{\rightleftharpoons}} [Cr(H_2O)_5(OOCCH(R)OH)]^{2+}$$

the values observed for k_f at 0.100 $\underline{M}$ $HClO_4$ and 25°C were very nearly identical (R = H, $k_f + 3.0 \times 10^{-2}$ $\underline{M}^{-1}$ sec^{-1};[10] R = CH_3, $k_f = 3.2 \times 10^{-2}$ $\underline{M}^{-1}$ sec^{-1}). In view of the similarity between the two systems, the tentative conclusions reached previously[10] are applicable here. It seems likely that the mechanisms parallel that presented for the analogous mercaptopropionate reaction. The higher rate of ring opening is reasonably attributable to the higher basicity of coordinated alkoxide _vs_ mercaptide.

It seems appropriate to recognize the similarity in spectral parameters for the chelated lactate and glycollate complexes in view of the discrepancy with earlier work mentioned by Lane.[10] These results with a very similar ligand provide further evidence of some error in the earlier report.[35]

Other Chromium(III) Systems

Similar substitution studies of the chromium(III) complexes with methylthioacetate and glycine were of secondary priority and work other than the identification of the reaction products of the initial oxidation-reduction was not attempted. It was noticed that, upon appropriate adjustment of the acidity to lower levels, $[Cr(H_2O)_5(OOCCH_2NH_3)]^{3+}$ reacts to yield an isolable product tentatively identified using spectral criteria as the chelate complex, _vide supra_.

Summary

This research has led to the following conclusions. (1) The incorporation of the carboxylate function in an appropriate chelate ligand can increase its bridging efficiency, apparently by increasing the steric accessibility of the carbonyl oxygen. (2) Cobalt(III) complexes in which a coordinated thioether function is the terminal donor in a chelate ligand can be prepared (conclusion reached jointly with Michael Gilroy). (3) A coordinated thioether function can serve as a bridging ligand in an inner-sphere reaction with an efficiency which is intermediate between highly efficient and poor bridging ligands. (4) The chromium(III)-thioether bond in the secondary chelate product of this reaction is quite labile. (5) The substitution of a methyl group for a hydrogen on the carbon adjacent to coordinated chalcogenide does inhibit inner-sphere reactivity but, surprisingly, by a similar factor ($\sim 1/40$) for both oxygen and sulfur. (6) As a result of the inhibition, the activation parameters for the mercaptopropionate system proved accessible and suggested from the high entropic barrier to reaction that the inhibition was steric in nature as anticipated. A comparison of the parameters with results obtained in this laboratory by co-workers permits a reasonable and internally consistent estimation of activation parameters for other reactions. Analyses of the variation in these parameters permit a much more detailed understanding of the electronic and steric contributions to the efficiency of coordinated mercaptide as a bridging ligand than was possible previously. To the extent that the estimates are valid

the high reactivity is derived mostly from the steric accessibility of the large sulfur atom. The lower reactivity of coordinated alkoxide complexes arises primarily from a lower accessibility of the smaller oxygen atom. (7) The presence of the adjacent methyl group apparently enhances the susceptibility of the pendant carbon-sulfur bond to lysis by coordinated hydroxide in the chromium(III) product. (8) Finally, we note the preparation of a number of new complexes via oxidation-reduction reactions. Thus, the objectives which were outlined for this research in the Introduction seem fulfilled.

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Frank Alexander Sedor was born in East Chicago, Indiana, on November 21, 1944. He graduated from Washington High School of East Chicago in 1962, and received the Bachelor of Arts degree with a major in chemistry from Wabash College, Crawfordsville, Indiana.

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Mr. Sedor is married to the former Judith Anne Dye of Crawfordsville, Indiana, and is the father of a daughter, Julia Christine, born, April 2, 1969.

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